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Molecular Reorientation of Some Fatty
Acids When in Contact With Water

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June, 1960

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MOLECULAR REORIENTATION OF SOME FATTY
ACIDS WHEN IN CONTACT WITH WATER

A thesis submitted by

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INTRODUCTION TO WETTING PHENOMENA

THE NATURE OF THE SOLID SURFACE

The surface of a solid shows properties which are not necessarily characteristic of its bulk. The fact that the molecules at the surface do not have neighbors in all directions gives rise to the unbalanced inward attraction which is responsible for the surface phenomena. The surface activity is evident from the phenomena of catalysis, adsorption, wetting, and many others.

The main difference between the solids and the liquids is that the molecules of the liquids can move rather freely while the molecules of the solids cannot. In view of the limited mobility of the molecules of the solids, surfaces are likely to be very complex in structure. Atoms or molecules tend to stay where they were when the surface was formed rather than move around and form a homogeneous surface. This, however, does not exclude a small degree of mobility which exists even in crystalline substances (1). The complexity of solid surfaces is due to heterogeneity which can be physical, chemical, or induced from foreign matter adsorbed on the surface.

The physical heterogeneity arises from the surface roughness and porosity of the solid. A surface is never entirely smooth on an atomic scale; but a more serious problem is usually provided by a larger scale roughness. This roughness provides a surface composed of crevices, declivities, edges or corners, and other irregularities. It is significant that each point of the solid surface may have different adsorbing ability depending on its location on the irregular pattern (2).

The chemical heterogeneity may arise from impurities adsorbed on the solid surface after the surface is formed or by simply being mixed with the solid during its formation. Defective structures may be due to lattice vacancies, to the presence of interstitial atoms, or to substitution of ions in the lattice.

The induced heterogeneity is due to changes that occur on a surface when the surface is partly covered with an adsorbed layer. The first molecules can have a decided effect on the energy with which the succeeding molecules are adsorbed. In chemical interactions especially, the interaction energy often decreases as coverage increases. Lateral attraction between adsorbate molecules may lead to increased energy of interaction between the adsorbed layer and the solid (2).

The study of solid surfaces is not an easy task. The main difficulty arises from contamination which is adsorbed or deposited on the surface during or after its preparation. A single molecular layer can alter the surface properties of a solid greatly. This is particularly true for solids with high surface activity. Ewald (3) has defined arbitrarily three possible types of solid surfaces:

- 1) The technical surface: one which has been in contact with air, organic vapors, and other contaminants.
- 2) The clean surface: one which has been subjected to rather extensive treatments such as washing, and heating under a moderate vacuum.

- 3) The pure surface: one which has been prepared in an extreme vacuum by splitting a crystal, etc., and then kept under conditions at which adsorption does not occur.

HIGH AND LOW ENERGY SURFACES

The unbalanced forces of the molecules at the surface of a substance give rise to the inward attraction of the surface whether liquid or solid. The work required to increase the surface by one area unit is called the specific free surface energy and it is mathematically equal to a hypothetical tension (surface tension) acting parallel to the surface of the substance.

Surfaces are usually classified into high and low energy surfaces. This classification, however, is only general in view of the fact that the two classes are not sharply distinguished but solids ranging from low to high energy exist. In general, if a surface has a high free surface energy, water will spread on it due to strong adhesional forces. Any type of contamination will reduce the free surface energy of a high energy surface, reducing the ability of the surface to be wetted. In the case of the low energy surface, little or no spreading of water occurs. Examples of high energy surfaces are metals such as platinum and copper. An example of low energy surface is paraffin. A high energy surface can be converted to a low one by adsorption of hydrocarbon or other low energy matter on this surface. A low energy surface, on the other hand, does not usually adsorb high energy matter so as to increase its free surface energy.

Most liquids should spread on clean metals and other inorganic high melting solids. This, however, is not always true experimentally. Zisman (4) claims that there are two main factors which account for the nonspreading of liquids on high energy surfaces. The first case is one where a liquid will not spread on its own surface (autophobic). The second case is one where the liquid is involved in a chemical change at the interface producing a low energy surface on which the bulk of the liquid will not spread. In the autophobic phenomenon the molecules of the liquid are wholly or in part polar-nonpolar (amphipathic) molecules. When they are placed in contact with a high energy surface the polar ends of the molecules are preferentially adsorbed at the solid surface leaving the non-polar ends extending into the liquid. This produces a low energy surface upon which the liquid will not spread. In the second case where chemical reaction takes place the new compound formed at the interface is a low energy compound which prevents spreading. The criterion for nonspreading is the same in both cases. That is, the surface tension of the liquid must be lower than the critical surface tension of the solid after adsorption or surface reaction. The critical tension of a solid is defined as that value of the liquid surface tension above which liquids show finite contact angles on the given surface (4).

The critical surface tension of the adsorbed layer is dependent on the closeness of packing and the chemical nature of the nonpolar end of the adsorbed molecules. When the molecules are unbranched, close-packed, and have terminal CH_3 , CF_2H , or CF_3 groups the critical surface tension is very low. When the molecules are branched or cyclic the critical surface tension is much higher in which case spreading of all but high surface energy liquids occurs.

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SURFACE FORCES AND WETTING

Wetting of a solid by a liquid can be defined as the interaction of the solid and the liquid. Such an interaction will, of course, depend on the surface forces of the interacting substances. Anything that would change the magnitude and direction of these forces would change the wettability or the interaction of the corresponding solid and liquid. The range of the surface forces has been a subject of great controversy but it is generally agreed that secondary valence forces act principally within atomic and molecular distances (1).

Langmuir (5) proposed a theory that the surface forces depend largely on the top layer of the groups of atoms which make up the surface and the atomic groups below that layer have very little or no effect on these forces. According to this theory the surface tension of pure liquids and the properties of adsorbed films at interfaces depend largely upon the orientation of the molecules in the interfaces. In a later reference (6) Langmuir made the observation that the so-called physical properties of nonpolar organic substances are usually roughly additive. For example, the addition of each CH_2 group to a hydrocarbon chain in most compounds containing such chains increases the volume, raises the boiling point, and alters the solubilities in approximately the same way. He reasoned from this observation that the field of force about any particular group or radical in a large organic molecule is characteristic of that group and, as a first approximation, is independent of the nature of the rest of the molecule. He referred to this as the principle of independent surface action. Thus, if a layer of closely

packed molecules of stearic acid are oriented in such a manner that all the CH_3 groups are on one plane and all the COOH groups are on another plane some 25 Å. away the wettability of the CH_3 plane should depend only on the forces between the liquid and the CH_3 groups and the wettability of the COOH plane should depend only on the forces between the liquid and the COOH groups.

The above discussion indicates that wetting should be described completely if the surface forces of the individual components are known. This, however, is not always true since the interaction effect between the liquid and the solid may not be additive in view of the possibilities of molecular reorientation and change in the electronic arrangement of the molecules or atoms at the interface.

Geometrical symmetry (similar atomic groups symmetrically arranged) of the molecules eliminates the effect of molecular reorientation at the interface but geometrical symmetry is not necessarily a sign of electronic symmetry. In reality, no molecule can be considered symmetrical in an asymmetrical field of force. The latter effect, however, may be negligible in which case the study of wetting is somewhat simplified. Some qualitative evidence of the influence of polarization on the surface energy of certain compounds is presented by Weyl (7) in a rather recent publication.

It can be seen from the above discussion that wetting of a solid depends primarily on the atomic groups which constitute the surface of the solid. This means that if the groups of atoms of the solid surface

change during the wetting process the wettability of the solid will change also. The wettability of a solid surface composed of different groups of atoms could conceivably be a summation of the interactions of the liquid and the different atomic groups of the solid. It should be realized that porosity and roughness of the solid surface will tend to complicate such a summation.

THE SIGNIFICANCE OF THE CONTACT ANGLE

Contact angle is the angle which a droplet of liquid makes with a solid and it is measured inside the liquid. Such an angle is taken as a measure of the wettability of the solid. For complete wetting the contact angle is zero; for no wetting the contact angle is 180° ; and for partial wetting the contact angle is some value between these two extremes. Unfortunately, the measurement of the contact angle is not an easy task, and quite often the actual angles observed do not accurately describe the thermodynamic quantities of surface energies. This could be attributed to changes occurring at the solid-liquid interface during the contact angle determination.

Unless special precautions are taken in preparing the surface, contact angles yield values which may vary between two rather wide limits. The lower value is the receding value and the larger is the advancing one. The existence of a range of contact angles has been termed hysteresis. According to Weiser (8) there are many factors which may influence hysteresis. Such factors are roughness of the surface, the presence of adsorbed films of foreign substances, which

are removed by the advancing fluid, and the formation of an adsorbed layer from the liquid or liquids used. If the solid surface is covered by a film of grease, vapor, or gas, its free surface energy may be lower than that of a pure solid. Thus, when a liquid boundary advances over the surface, it yields an abnormally high angle. However, if this film can be dissolved into the liquid droplet, the receding angle will be lower than the advancing angle.

Molecular orientations at the surface can greatly influence contact angles. Many molecules contain both hydrophobic and hydrophilic groups. Excellent examples of this are the fatty and resin acids. If the surface contains many carboxyl groups, the contact angle with water or other polar liquid will be low. If, on the other hand, the carboxyl groups are buried in the solid, and remain there, the water will exhibit a stable high contact angle.

Although a change in the contact angle can take place only by changing the individual and interfacial free surface energies the ways by which these quantities can be altered are numerous. The list that follows shows some of the important experimental factors encountered in carrying out such measurements.

1. Adsorption at any phase boundary.
2. Heterogeneity of the surface structure.
3. Reaction between phases.
4. Electrostatic effects.
5. Surface roughness and porosity.
6. Velocity of movement of liquid over a solid.

7. Previous treatment of the solid (heat, etc.).
8. Method of bringing the phases into contact.
9. Vaporization from the liquid phase.

The numerous list of experimental difficulties involved in measuring contact angles may give little hope for the significance of the contact angle. This, however, does not invalidate the angle for certain systems where the conditions are carefully controlled or comparative results are desired. The contact angle is quite reproducible for low energy homogeneous solids where adsorption of moisture and impurities are insignificant. The results of Inaba (9) on purified paraffin show comparatively little hysteresis for such a system.

In spite of all the problems involved in the measurement of a contact angle, it still remains the most important fundamental quantity of wetting and its measurement under controlled conditions can prove of great value.

QUANTITATIVE TREATMENT OF IDEAL SOLID SURFACES

Under static conditions wettability may be defined as the "equilibrium" free energy of adhesion between a liquid and a solid (10). This quantity may be determined by Equation (1) which is known as the Dupré equation. Fox and Zisman (11, 12) have given a good treatment of the quantitative aspects of wetting and the following analysis has been gleaned largely from their papers.

$$W_A = \gamma_{SO} + \gamma_{LVO} - \gamma_{SL} \quad (1)$$

where, W_A : Work of adhesion or work required to form a unit area of pure solid and pure liquid surface.

γ_{S^0} : Specific surface energy of the pure solid measured in an absolute vacuum.

γ_{LV^0} : Specific surface energy of the liquid measured in its saturated vapor.

γ_{SL} : Specific solid-liquid interfacial free energy.

Equation (1) is not very useful as such in view of the difficulties encountered in determining the quantities γ_{S^0} and γ_{SL} . These difficulties, however, can be overcome by assuming Equation (2), known as the Young equation, to be valid:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \quad (2)$$

This equation describes the equilibrium condition for the solid, liquid, and gas interfaces. In order to account for saturated conditions these changes must be made in the symbols.

$$\gamma_{SV^0} = \gamma_{SL} + \gamma_{LV^0} \cos \theta_E \quad (3)$$

where, SA: solid-air interface

SL: solid-liquid interface

LA⁰: liquid-air interface

SV⁰: solid-vapor interface (at saturated pressure P⁰)

LV: liquid-vapor interface (at vapor pressure P)

θ_E : equilibrium contact angle in saturated vapor.

When the vapor pressure is less than the saturation pressure and the contact angle does not change with time as a result of vapor adsorption the sub and superscripts are dropped.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_E \quad (4)$$

From Equations (1) and (4) one obtains

$$\frac{W_A}{A} = \gamma_{SO} - \gamma_{SV} + \gamma_{LV0} \left(1 + \frac{\gamma_{LV}}{\gamma_{LV0}} \cos \theta_E\right) \quad (5)$$

$$\text{or } \frac{W_A}{A} = \pi + \gamma_{LV} (1 + \cos \theta_E) \quad (6)$$

where, $\pi = \gamma_{SO} - \gamma_{SV}$ = surface spreading pressure and

$$\gamma_{LV} \approx \gamma_{LV0}$$

The simplifying assumption, $\gamma_{LV} \approx \gamma_{LV0}$, is closely approximated for liquids of low vapor pressure.

It is thought that the free surface energy change of a low energy solid when it is placed in contact with the saturated vapor is small. The free energy decrease on immersion of a solid in a saturated vapor, f_{SV0} , is numerically equal to the equilibrium pressure π_E .

$$\frac{W_A}{A} = f_{SV0} + \gamma_{LV0} (1 + \cos \theta_E) \quad (7)$$

If f_{SV0} is assumed to be zero or negligible, Equation (7) reduces to

$$\frac{W_A}{A} = \gamma_{LV0} (1 + \cos \theta_E) \quad (8)$$

Equations (7) and (8) are working equations for evaluating the wettability of a solid provided the quantity f_{SV0} can be neglected or determined. Unfortunately, f_{SV0} is not simply determined experimentally. Bangham (13) has shown that this quantity, the free energy decrease on immersion of the solid in the saturated vapor, can be calculated from the adsorption isotherm of the solid vapor system by integrating Gibb's

adsorption equation from zero pressure to the saturation pressure of the vapor. Thus,

$$f_{SV^0} = \frac{RT}{\Gamma} \int_0^{P^0} \Gamma d \ln P \quad (9)$$

where, R : the gas constant

T : the absolute temperature

P^0 : the saturation pressure in dynes per square centimeter

Γ : the surface concentration of the adsorbed molecules
in moles per square centimeter

In the case of volatile liquids the correction could be quite significant. However, for water at 20°C., the saturated pressure is so low that the correction becomes negligible, unless the adsorbents are hygroscopic. This fact justifies the use of Equation (8) for water and most solids.

A further deduction from the equation stated above is an expression for the free energy change upon immersion of a solid into a liquid. If γ_{SO} is added to both sides of Equation (3), the following expression is possible upon rearrangement of the terms.

$$(\gamma_{SO} - \gamma_{SL}) - (\gamma_{SO} - \gamma_{SV^0}) = \gamma_{LV^0} \cos \theta_E \quad (10)$$

$$\text{or} \quad \gamma_{SO} - \gamma_{SL} = \pi_E + \gamma_{LV^0} \cos \theta_E \quad (11)$$

But $\gamma_{SO} - \gamma_{SL} = f_{SL}$ = free energy decrease of immersion of the solid in the liquid

$$\text{and} \quad f_{SL} = f_{SV^0} + \gamma_{LV^0} \cos \theta_E \quad (12)$$

If f_{SV^0} is negligible, Equation (12) reduces to (13) which is a simplified working equation.

$$f_{SL} = \gamma_{LVO} \cos \theta_E \quad (13)$$

Wetting has also been defined as the tendency of the liquid to spread on the solid. The difference between the work of adhesion and the work of cohesion, the latter referring to the work necessary to separate a unit area of liquid from itself, is taken as a measure for the tendency of the liquid to spread on the solid and it is called the spreading coefficient. If the work of cohesion (twice the surface tension of the liquid) is equal or less than the work of adhesion the liquid is attracted to the solid more than to itself, and it will spontaneously spread over the solid surface; consequently, θ_E will be zero. On the other hand, if the work of cohesion is greater than the work of adhesion the liquid molecules are attracted to themselves more strongly than to the solid and θ_E will be finite, allowing for partial wetting but not complete spreading. As the work of adhesion approaches zero for constant values of the work of cohesion the contact angle will approach 180° . It is known, however, that all molecules have some attraction for each other so that θ_E can never be 180° for a smooth and nonporous solid.

The validity of the above relations depends on the validity of the assumptions made. The first assumption made is that the Young equation describes the solid-liquid-vapor interfaces. This equation has been the subject of many criticisms (14). Johnson (15) in a recent publication has shown that the Young equation is valid provided surface tensions are used rather than surface energies. He claims that the surface energy is not numerically equal to the surface tension for all systems. Collins and Cooke (16) in another recent publication concluded that the equation

is sound using free surface energies. It seems that there should not be much question about the validity of the equation in systems where the surface energies are mathematically equal to the surface tensions. This is undoubtedly the case for molecularly smooth solids where no adsorption of a third component takes place.

The second assumption is that the surface tension of the liquid in air is equal to the surface tension of the liquid in its saturated vapor. Fox and Zisman (12) have demonstrated that the contact angles of the higher boiling liquids on the low energy surfaces are the same in air as in air saturated with vapor. This supports the second assumption that $\gamma_{LA} \approx \gamma_{LV}$, at least for the higher boiling nonspreading liquids. The third assumption is that the free energy decrease on immersion of the solid in the saturated vapor is negligible. This assumption can be given some support by considering the nature of low energy surface. Since the free surface energy is low, the surface will have a low adsorptivity for the vapor in contact with it. Also, if the surface energy is low initially, low energy vapors will produce only a minor effect. Large changes, however, can occur if the surface is initially a high energy surface. Fox and Zisman (17) have shown that the adsorption of n-alkane vapor on paraffin has little effect on the free surface energy of the paraffin.

THE EFFECT OF ROUGHNESS AND POROSITY ON WETTING

The quantitative aspects of the wetting theory already discussed assume smooth and homogeneous surfaces. This, however, is seldom true since many apparently smooth surfaces have cracks, fissures, and other

irregularities. The effect of roughness on wetting was first studied quantitatively by Wenzel (18) who hypothesized that the actual area of the solid and not the geometrical area was the important area to be considered.

The effect of roughness may be understood if one realizes that the Young equation refers to plane geometrical unit areas. Liquids will conform to this, but few solids will. In other words, the free surface energy change of a rough solid immersed in a liquid will differ from that of a unit plane geometrical surface. The difference will depend upon the ratio, A_1 , of actual surface to plane surface area. The free energy change in forming a liquid-solid interface will then be $A_1(\gamma_{SVO} - \gamma_{SL})$, and the Young equation will be modified to read

$$\cos \theta_A = \frac{A_1 (\gamma_{SVO} - \gamma_{SL})}{\gamma_{LV}} = \frac{A_1}{\gamma_{LV}} \cdot \cos \theta_E \quad (14)$$

where θ_A is the apparent contact angle measured on a rough surface and θ_E is the true contact angle measured on a smooth nonporous surface. In other words, then, the effect of roughness is to increase the apparent advancing contact angle when the actual advancing contact angle is obtuse, and to decrease the apparent advancing contact angle when the actual advancing contact angle is acute.

Cassie and Baxter (19) have shown both theoretically and experimentally that when water is placed upon a carefully constructed grid of paraffin-coated wires, the apparent contact angle can be much greater than the actual contact angle. These workers showed that when the distance between parallel wires of a coated grid was twice the diameter of the wires, the apparent contact angle was 143° , although the actual

contact angle was only 105° . They point out the fact that a duck gains its excellent water repellency by virtue of the structure and spacing of the feathers, and not because of some superlative sizing agent.

This may be understood if free surface energy changes are considered. Let A_1 be the total area of the solid-liquid interface and A_2 be the total area of the liquid-air interface in a plane of geometrical area of unity parallel to the rough and porous surface. The net energy change in covering this unit plane area of rough and porous surface with the liquid can be expressed as

$$\underline{E}_D = A_1 (\gamma_{SL} - \gamma_{SVO}) + A_2 \gamma_{LVO} \quad (15)$$

Combining the Young equation with Equation (15)

$$\underline{E}_D = \gamma_{LVO} (A_2 - A_1 \cos \theta_E) \quad (16)$$

Equation (3) or the Young equation may also be written

$$\cos \theta_E = -\underline{E} / \gamma_{LVO} \quad (17)$$

where \underline{E} is the energy required to form a unit area of the solid-liquid interface. An apparent advancing contact angle for a rough and porous surface may then be defined by

$$\cos \theta_D = \underline{E}_D / \gamma_{LVO} = A_1 \cos \theta_E - A_2 \quad (18)$$

Equation (18) shows that whereas surface roughness can either increase or decrease the apparent contact angle, the porosity of a surface will always increase the contact angle. Roughness and porosity are closely related terms as far as wetting is concerned for the reason that a drop-let may not distinguish between surface depths and pores (this is

definitely true when the contact angle is greater than 90°). This follows from the fact that the molecular forces are short-range forces and cannot extend through pores and depths. This may be the reason for failures, encountered in the literature, to verify Wenzel's expression in the form of Equation (14) where only roughness is considered and the liquid-air interface between the liquid and the solid is ignored (20).

Although the above quantitative treatment has proved very useful in many instances, it still lacks universal applicability. The subject of roughness is not only a matter of actual area of the solids but the type of grooves and shape of crevices are also important. The grooves and crevices of the actual surface act as small capillaries and consequently the water will curve either towards the solid surface or away depending on the true contact angle of water on a smooth and nonporous surface. This form of capillarity will determine the total solid-liquid and liquid-air interfaces when water comes in contact with the rough and porous solid in the absence of gravitational effects. The total energy change upon contact of the water on the solid will be described by Equation (15) provided only surface energies are involved.

INTRODUCTION TO THE PROBLEM

PRESENTATION OF THE PROBLEM

Wettability data for many systems are found in the literature but very few systems give reliable and reproducible results. It has been observed that the angle of contact, under static conditions where evaporation is controlled, of many systems decreases with time. This presupposes not only differences from point to point on the solid surface but also changes occurring at a particular point as a result of the water proximity. The reasons for the changes in the contact angle are not clear but the possibilities of moisture adsorption, spreading of the solid, and molecular reorientation are present. Thus, wetting is not necessarily a phenomenon of instantaneous equilibrium but a rate phenomenon where energies of activation of significant magnitude may be involved. A change at the interface is not necessarily the formation of a new chemical compound between the wetting liquid and the solid substrate but a geometrical reorientation of the solid molecules at the interface is sufficient to alter the wetting properties of the solid. Such a reorientation presupposes breaking of bonds of the molecules of the solid from each other so that they can move and take positions which are energetically stable in the presence of the new field. The energy which is required to overcome the cohesive energy of the molecules of the solid could conceivably be the energy of activation for such a change.

Inaba (9) and Rideal and Tadayan (21) have reported contact angle measurements for water on paraffin-palmitic acid and paraffin-stearic acid mixtures, respectively. The studies include the effect of interfacial aging between solid and water on the contact angle. The observed

decrease in contact angle with interfacial aging is explained by assuming a reorientation of the acid molecules of the solid mixture so that the hydrophilic carboxyl groups face the water and increase the wettability of the solid. The interfacial aging required for the decrease in contact angle is appreciable and warrants a study from the kinetic point of view. The results of the systems studied indicate strongly that molecular reorientation occurs but further studying from the equilibrium and kinetic points of view are necessary. It is thought that a study of molecular reorientation and the rate at which the molecules move will prove valuable to the hypothesis of reorientation. Thus, the objectives of this thesis can be stated as follows:

1. To provide further evidence which will strengthen or weaken the hypothesis that the molecules at the top layer of the solid fatty acid reorient themselves when water comes in contact with the acid.
2. To study the phenomenon of molecular reorientation of fatty acids in a quantitative fashion by studying the kinetics and equilibrium of the reaction.

Fatty acids are ideal substances for studying wettability because the solid-air interface is a very low energy surface which minimizes chances of contamination and adsorption. Furthermore, the use of molecular deposition allows for rather smooth and nonporous surfaces of thickness as low as the molecular length. This technique was used to prepare the surface for the wettability study of this investigation. The fatty acids to be studied were limited to stearic, myristic, and lauric. Other fatty substances of low surface energy like stearyl

alcohol and paraffin were used for studying specific points of this investigation.

BACKGROUND OF THE PROBLEM

Hardy (22) pointed out that the surface of molten stearic acid would present to a dry air phase only hydrocarbon chains, since the polar heads would bury themselves in the medium of higher dielectric constant, namely, the molten acid. If, on the other hand, the molten acid is in contact with water the polar groups of the acid will have a tendency to turn to the aqueous phase. Adam and Jessop (23) observed that pure long-chain acids and alcohols, solidified in contact with air, showed contact angles against clean water as large as 100° which is almost the angle obtained for paraffin wax. If a cut was taken through the solid mass, the contact angle of the surfaces so exposed proved to be as low as 50° . This is important because it supports Hardy's idea about molecular orientation at the surface and Langmuir's idea that the forces determining the contact angle are short-range forces.

Hardy's remarks were studied experimentally by Nietz (24) who measured the angle of contact on stearic acid crystallized in the presence of water and found that it was greatly reduced. Pockels (25) extended Nietz's work to other compounds and found that their wettability increased significantly after being in contact with water for variable lengths of time if the compound contained polar groups but it was unchanged in substances like shellac and wax which contain

no polar groups. Kneen and Benton (26) studied the wettability of stearic and palmitic acid surfaces formed in air and in contact with glass and found that the air-formed surface had a contact angle of 105° while the surface formed in contact with glass had a contact angle of 71° for palmitic acid and 64° for stearic acid. They explained the results by assuming that the surface formed in contact with glass was highly oriented with the carboxyl groups facing outward.

Langmuir (27, 28) studied the orientation of oleic acid monolayers on different solids and the dependence of the contact angle on this orientation. He found that the surfaces became hydrophobic, upon the deposition of the acid monolayer, and the contact angles depended greatly upon the character of the underlying solid. The angle was 18° for mica, 45° for glass, 65° for platinum, 70° for calcite, 82° for sphalerite, and 86° for galena. He explained these results by assuming that on galena, with its strong field of force, the active groups of the acid are held so firmly that water cannot cause an appreciable fraction of them to change their orientation. With a monolayer on glass, on the other hand, the presence of the overlying drop of water may bring some of the active groups to the upper surface of the film so that the water spreads over this surface much more easily than over paraffin, giving a much lower contact angle. Langmuir's experiments indicate that the fraction of the monolayer which overturns can be appreciable if the substrate is a substance of weak field of force. Thus, the underlying solid substrate does not directly influence the contact angle but determines the

degree of orientation of the deposited monolayer which in turn determines the magnitude of the contact angle. Another finding of Langmuir's experiments (29) was the fact that a hydrophobic fatty acid surface could become hydrophilic by conditioning the surface with multivalent cations of thorium or aluminum salts. He explained this phenomenon by assuming that the top molecular layer was reoriented so that the carboxyl groups were facing outward.

✓ Schacht, Scheibe, and Schuller (30) studied the wettability of stearic acid monolayers on several solids and found that the contact angle for a monolayer on glass and mica decreased rather rapidly while the contact angle for a monolayer on copper remained practically constant with time. The results are interpreted by mentioning the possibility of molecular reorientation.

Inaba (9) studied the wettability of palmitic acid-paraffin mixtures as a function of time of interfacial aging under conditions where the water surface was constantly cleaned. The results show a decrease in the angle of contact over a period of twenty-four hours or more. More recently Rideal and Tadayon (21) studied the wettability of paraffin-stearic acid mixtures and the effect of interfacial aging on the wettability by allowing the droplet to age over the surface of the mixture. The results show that the increase of stearic acid in the mixture decreases the contact angle considerably with interfacial aging. They further found that if a monolayer deposited on a solid substrate came in contact with a clean solid surface for a prolonged period, it was partitioned by transferring of molecules from the monolayer to the clean surface. The partition coefficients varied depending

on the substrate solids used. Equal partition was observed if the two solids were identical and no chemical reaction was involved. This indicates that molecular movement is taking place at the interface of the monolayer and a shift in equilibrium occurs when another substance approaches the monolayer.

Ray, Anderson, and Scholz (31) in a recent publication studied the wetting angle of water and organic liquids on polysaccharide films whose surfaces had been cast on substrates of different polar character. The data show that films cast on polar surfaces were more hydrophilic than those cast on nonpolar surfaces. Different substrate surfaces would induce different amounts of orientation and different surface concentrations of hydroxyl groups, depending on the polarizing effect of the particular solid.

Summarizing the above discussion one can list the following observations which have been explained by the assumption of molecular reorientation.

1. A solid composed of polar-nonpolar molecules becomes more wettable if crystallized in the presence of water.
2. The wettability of polar-nonpolar compounds increases if the compounds are conditioned with water for a length of time.
- ✓ 3. The wettability of a solid covered with a monolayer of fatty acid depends on the character of the substrate solid.
4. The wettability of polysaccharide films cast on substrates of different polar character increases with the polarity of the solid substrate.

- ✓ 5. A hydrophobic stearic acid surface can be converted to a hydrophilic one by conditioning it in a solution of certain multivalent cations.

AN APPROACH TO THE PROBLEM

THEORETICAL CONSIDERATIONS

It was mentioned earlier that the phenomenon of wetting is not necessarily a case of instantaneous equilibrium but a rate phenomenon where appreciable energies of activation may be involved. It was also mentioned that in the light of the experimental evidence substances composed of amphipathic molecules show a large difference between the initial and the equilibrium contact angle. The theory of molecular reorientation has been proposed by several investigators to explain such differences in the contact angle. Molecular reorientation can be conceived as a rate phenomenon since time will be required for the molecules to break the cohesive bonds from their neighbors and become free for taking new positions. It is the purpose of this section to explore theoretically the possibility of the reorientation phenomenon and try to predict the extent and the rate of the reaction. The three fundamental questions which will have to be answered are:

1. Can the reaction take place or more correctly is the reaction thermodynamically favored?
2. To what extent is the reaction taking place or what is the equilibrium constant?
3. How fast is the reaction proceeding or what is the rate constant of the reaction?

Satisfactory answers to the above questions will describe the reaction of molecular overturning in a general fundamental sense.

THERMODYNAMIC PROBABILITY OF REORIENTATION

No reaction is completely possible or completely impossible. The problem is one of probability and as such the two questions of possibility and extent of the reaction can be treated as one.

The thermal equilibrium of any process is established when the distribution of molecules in the regions under consideration is such that the free energy is minimum. The number of molecules \underline{n}_1 having energy \underline{e}_1 per molecule is given by the Boltzmann distribution equation

$$\underline{n}_1 = \underline{g}_1 \exp(-\alpha) \exp(-\underline{e}_1/kT) \quad (19)$$

where, \underline{n}_1 = number of molecules having energy \underline{e}_1

\underline{g}_1 = statistical factor

α = a constant

k = Boltzmann constant

T = absolute temperature

If two regions are considered, the ratio $\underline{n}_1/\underline{n}_2$ is equal to the ratio of the absolute probabilities $\underline{P}_1/\underline{P}_2$ for the existence of the molecules in the two states and is given by

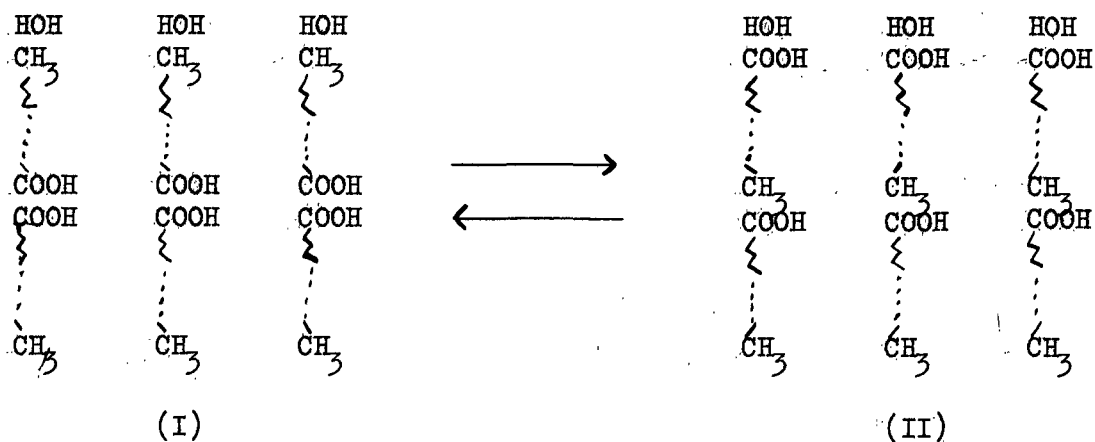
$$\underline{P}_1/\underline{P}_2 = [\underline{g}_1 \exp(-\alpha_1)/\underline{g}_2 \exp(-\alpha_2)] \exp(\underline{\Delta E}/RT) \quad (20)$$

where \underline{g}_1 , \underline{g}_2 , α_1 , and α_2 are constants. $\underline{\Delta E}$ is the difference in potential energy of the molecules in the two regions (molar basis), and R is the gas constant. The ratio $[\underline{g}_1 \exp(-\alpha_1)/\underline{g}_2 \exp(-\alpha_2)]$ for geometrically similar situations is, for all practical purposes, equal to unity. Thus, Equation (20) can be simplified to read

$$\underline{n}_1/\underline{n}_2 = \underline{P}_1/\underline{P}_2 = \exp(\underline{\Delta E}/RT) \quad (21)$$

Equation (21) can be applied to study the probability of orientation of molecules in contact with a liquid or solid surface provided the energy term ΔE is known. ΔE may be considered to be equal to the difference of the interfacial tensions of the molecules in the two regions. Such an approach was used by Langmuir to establish the orientation of molecules at a methanol/air interface (32).

Let us see now how the above analysis can be applied to the present situation where a polar liquid (water) is in contact with a multilayer of amphipathic molecules (stearic acid). The schematic diagram shown below indicates two possible states of the stearic acid molecules in contact with water.



State (I) is the initial position of the molecules and there is not much question about the molecular arrangement since x-ray diffraction patterns and surface properties have provided sufficient evidence for such an arrangement (33). State (II) is the alternative position of the molecules if molecular overturning takes place.

Surface energy considerations reveal that the interfacial energy of the molecules in state (I) is simply the interfacial energy of

water and methyl groups $\gamma_{\text{H}_2\text{O}-\text{CH}_3}$ but the interfacial energy of the molecules in state (II) is the sum of two interfacial tensions $\gamma_{\text{H}_2\text{O}-\text{COOH}}$ and $\gamma_{\text{CH}_3-\text{COOH}}$. Thus, the standard molar free surface energy (ΔF°) for the reaction will be

$$\Delta F^\circ = \frac{A}{N} (\gamma_{\text{H}_2\text{O}-\text{COOH}} + \gamma_{\text{CH}_3-\text{COOH}} - \gamma_{\text{H}_2\text{O}-\text{CH}_3}) \quad (22)$$

where A is Avogadro's number and N is the number of molecules per square centimeter. The standard free energy is also related to the equilibrium constant (K) by the following expression:

$$-\Delta F^\circ = RT \ln K \quad (23)$$

where $K = \frac{n_{\text{II}}}{n_{\text{I}}}$ and n_{I} and n_{II} are the number of molecules in states (I) and (II). Thus, if the interfacial tensions are known the calculation of the equilibrium constant becomes possible.

Direct measurement of the interfacial tension for two liquids is possible but the interfacial tension between a solid and a liquid cannot be determined by direct experimentation. The interfacial tension of two mutually saturated liquids a and b is approximated by Antonow's rule which states that the interfacial tension is simply the difference of the surface tensions of the two components (1, 53). ✓

$$\gamma_{ab} = \gamma_a - \gamma_b \quad (24)$$

This rule stems from Laplace's picture of tensions at phase boundaries and it obviously is a logical statement when interaction effects are neglected. There has been much argument with regard to the validity of the above rule and this is due to inappropriate use of the rule or not

knowing the magnitude of the interaction effects involved. When two liquids come in contact there are at least two types of interactions which must be considered. The first is geometrical and the second is electronic. When the molecules are not symmetrical a change in the orientation of the molecules at the surface may take place. This can influence the interfacial tension considerably since surface forces are active within atomic distances. In addition, the contact of one surface with another will influence the electronic symmetry of the atoms or molecules at the surface and may alter the surface energies of the individual components. This probably happens with all types of molecules but the seriousness of such an effect will depend on the type of molecule. The effect can be considered negligible for molecules of dissimilar nature and generally small for most types of molecules. To illustrate the point regarding Antonow's rule let us consider the following two systems:

a) water-octane

$$\gamma_{H_2O} = 72.5 \text{ erg/cm}^2 \quad (14)$$

$$\gamma_{\text{octane}} = 21.8 \text{ erg/cm}^2 \quad (34)$$

$$\text{calculated } \gamma_{H_2O\text{-octane}} = 50.7 \text{ erg/cm}^2$$

$$\text{experimental " " } = 50.0 \text{ erg/cm}^2 \quad (14)$$

b) water-butyl alcohol

$$\gamma_{H_2O} = 72.5 \text{ erg/cm}^2$$

$$\gamma_{\text{butyl alc.}} = 27.4 \text{ erg/cm}^2 \quad (14)$$

$$\text{calculated } \gamma_{H_2O\text{-butyl alc.}} = 45.1 \text{ erg/cm}^2$$

$$\text{experimental " " } = 1.6 \text{ erg/cm}^2 \quad (14)$$

It is seen that the rule applies to the water-hydrocarbon system but it fails in the water-alcohol system. In the first case the actual contact is mainly between water molecules and hydrocarbon groups but in the second case the contact is between water, OH, CH₂, and CH₃ groups (water and OH groups is probably the main contact area). It is thought, however, that the molecular groups in contact determine the interfacial tension and not all parts of the molecule. Therefore, Antonow's rule would probably apply to most systems if only the surface energies of the groups of atoms in contact are considered and not the whole molecule. The surface tension of butyl alcohol in air is determined by the surface tension of the outer groups which are mainly CH₃ groups; but when the alcohol is in contact with water the outer groups are no longer CH₃ but OH, CH₂, and CH₃. In other words, the orientation of the outer layer of alcohol molecules is different when in contact with water.

Thus, Antonow's rule will definitely fail when amphipathic molecules come in contact with water unless the orientation effect is taken into account. It should be mentioned that Carter and Jones (54) found that the rule is quite applicable if the surface tensions are measured after the liquids are mutually saturated. Thus, the difference between the calculated and the experimental interfacial tensions is quite small if water is saturated with alcohol and vice versa. For liquids which are practically insoluble in each other (long-chain acid and water) any deviation could be attributed to reorientation of the molecules at the interface.

Another reason for failure of Antonow's rule is the possibility of impurities at the interface.

If the surface energies of the groups of atoms are known the use of Antonow's rule is quite helpful in calculating the interfacial tensions. A good approximation of the surface energy of atomic groups can be made from the cohesive energies given by Mark (35) for several organic groups:

Group	Cohesive Energy in Cal./Mole, $\underline{W_c}$
-CH ₃	1780
-CH ₂	990 (only approximately known)
-COOH	8970
-OH	7250

Since the cohesive energy $\underline{W_c}$ is twice the surface energy value the surface energies of the groups are as follows¹:

$$\begin{aligned}\gamma_{CH_3} &= (1780) [(1/2) \{1/(6.02 \times 10^{23})\} (5.4 \times 10^{14}) (4.185 \times 10^7)] \\ &= (1780)(1.88 \times 10^{-2}) = 33.4 \text{ erg/cm.}^2\end{aligned}$$

$$\gamma_{CH_2} = (990)(1.88 \times 10^{-2}) = 18.5 \text{ erg/cm.}^2$$

$$\gamma_{COOH} = (8970)(1.88 \times 10^{-2}) = 150.0 \text{ erg/cm.}^2$$

$$\gamma_{OH} = (7250)(1.88 \times 10^{-2}) = 136.0 \text{ erg/cm.}^2$$

Using Antonow's rule the interfacial tensions for the different groups are:

$$\gamma_{H_2O - CH_2} = 72.5 - 18.5 = 54.0 \text{ erg/cm.}^2$$

$$\gamma_{H_2O - CH_3} = 72.5 - 33.4 = 39.1 \text{ erg/cm.}^2$$

$$\gamma_{COOH-CH_3} = 150.0 - 33.4 = 117.6 \text{ erg/cm.}^2$$

$$\gamma_{H_2O - COOH} = 72.5 - 150.0 = -77.5 \text{ erg/cm.}^2$$

¹ Each numerical value is calculated using

$$\gamma = 1/2 \underline{W_c} [\{ (\text{no. of molecules per sq. cm.}) / (\text{Avogadro's no.}) \} (\text{erg/cal.})]$$

$$\gamma_{\text{COOH-CH}_2} = 150.0 - 18.5 = 131.5 \text{ erg/cm.}^2$$

$$\gamma_{\text{H}_2\text{O-OH}} = 72.5 - 136.0 = -63.5 \text{ erg/cm.}^2$$

$$\gamma_{\text{OH-CH}_3} = 136.0 - 33.4 = 102.6 \text{ erg/cm.}^2$$

The negative surface energies are not contrary to known facts and they express the very strong effects of these radicals in increasing the solubility of organic substances in water.

Since the values are obtained from cohesive energies they will be the values which a surface will have under the influence of a similar field. This, of course, tends to minimize the effects of electronic interaction when two rather similar groups come into contact. Langmuir (32) attempted to relate the interfacial energies of the atomic groups to the vapor pressure of single components and binary mixtures but the interfacial tensions used are not reliable as pointed out by Smythe and Engel (36) who suggest a value 97.5 erg/cm.^2 for $\gamma_{\text{CH}_3-\text{OH}}$ in butyl alcohol rather than 33.7 erg/cm.^2 used by Langmuir. This compares well with the value calculated using cohesive energies and Antonow's rule (102.6 erg/cm.^2).

From the above analysis one can easily see that the molecules in the initial state (I) are energetically equivalent to the molecules in the final overturned state (II) or

$$\Delta F^0 = (\gamma_{\text{H}_2\text{O-CH}_3}) - (\gamma_{\text{H}_2\text{O-COOH}} + \gamma_{\text{COOH-CH}_3}) = 0$$

Since ΔF^0 is equal to zero the relative probability of the molecules to exist in either state is 50% or that one half of the molecules will overturn if sufficient time is allowed.

THE KINETICS OF REORIENTATION

The previous discussion has shown that the reaction is thermodynamically possible but says nothing about the rate at which such a reaction takes place. The first question that comes to mind is whether the molecules in the solid state are capable of any mobility. Pauling (37) states that certain polymorphic changes in crystals, accompanied by absorption of heat, could be explained on the assumption that the molecules constituting the lattice commenced to rotate freely at a particular temperature when the crystal was heated. At low temperature the energy of rotation may be insufficient to overcome the lattice forces and the molecules will undergo an oscillatory, or to and fro, rotation, i.e., libration. The most direct evidence for detecting such molecular mobility is crystal structure and dielectric constant, although the variation of specific heat and thermal expansion with temperature have provided valuable information. The fact that solids have vapor pressure is proof that molecular mobility in the solid state exists. Some kind of mobility should be expected at any temperature above the absolute zero.

The rate at which the present reaction takes place will depend on the ease of mobility of the stearic acid molecules which in turn will be a function of the temperature and the cohesive forces between the molecules. Rideal (38) and Eyring (39) have suggested that Eyring's absolute reaction theory (49) may be applicable to this particular problem:

$$k' = (kT/h) \exp (-\Delta F^*/RT) \quad (25)$$

where, $\underline{k'}$ = specific reaction constant
 \underline{k} = Boltzmann constant (1.380×10^{-16} erg/deg.)
 \underline{h} = Planck's constant (6.6238×10^{-27} erg-sec.)
 $\underline{\Delta F^*}$ = free energy of activation
 \underline{R} = gas constant (1.987 cal./mole/deg.)
 \underline{T} = absolute temperature

Remembering that the free energy of activation can be given by

$$\underline{\Delta F^*} = \underline{\Delta H^*} - \underline{T} \underline{\Delta S^*} \quad (26)$$

the rate constant equation takes the following form:

$$\underline{k'} = (\underline{kT}/\underline{h}) \exp [(-\underline{\Delta H^*}/\underline{RT}) + (\underline{\Delta S^*}/\underline{R})] \quad (27)$$

where $\underline{\Delta H^*}$ = total energy of activation

$\underline{\Delta S^*}$ = entropy of activation

If Equation (27) is to be utilized the quantities $\underline{\Delta H^*}$ and $\underline{\Delta S^*}$ will have to be calculated in some manner. If a molecule is to move, it must become free from the restraint exerted by its neighbors. That is to say, the physical bonds of each molecule and its neighbors must be broken. Once that happens the molecule is free to take many shapes and spatial configurations so that rotation is possible. Thus, it is conceivable that the heat of activation is equal to the cohesive energy of the individual molecule. This would amount to about 25,000 cal./mole for stearic acid, 23,000 cal./mole for palmitic acid, 21,000 cal./mole for myristic acid, and 19,000 cal./mole for lauric acid.¹

It is very difficult to predict the entropy of activation since the partition functions of the molecules are not known. Calculation

¹ The cohesive energy for each acid is calculated from the cohesive energies of the atomic groups presented earlier.

of the partition functions requires knowledge of the configuration of the molecules in the activated state which is not available. Thus, only rough estimates of the kinetics can be made utilizing the cohesive energy of the acid and neglecting the entropy of activation. Table I shows such estimates for several acids.

TABLE I

ESTIMATED RATE CONSTANTS FOR MOLECULAR
MOBILITY OF FATTY ACIDS AT 25°C.

Fatty Acid	Carbon Atoms	Cohesive Energy, cal./mole	Specific Rate Constant, sec. ⁻¹
Stearic	18	25,000	2.98×10^{-6}
Palmitic	16	23,000	0.84×10^{-4}
Myristic	14	21,000	2.46×10^{-3}
Lauric	12	19,000	7.26×10^{-2}

The values calculated above are not expected to be absolute values in view of the simplifying assumptions involved. They show, however, the effect of chain length on the mobility of the molecules. The exponential nature of the kinetics shows that a small increase in the length of the molecule can decrease the rate manifold. A significant effect is expected also if the temperature is varied.

EXPERIMENTAL APPROACH TO THE PROBLEM

The above discussion has shown that molecular reorientation of fatty acids in contact with water is possible and that the rate of such a process depends on the cohesive energy and the length of the molecule. It is necessary now to design experiments which will provide

qualitative and quantitative information regarding the phenomenon of reorientation.

The general method for studying this problem is that of wettability of a fatty substance deposited on a solid substrate. Since the wettability of a surface depends on factors other than reorientation, it is necessary to define the experimental conditions and separate the different variables. Such other variables are moisture adsorption and spreading of the solid. Both of these factors will be considered later.

If a monolayer of fatty acid is deposited on a metal substrate by the Langmuir technique (to be described later) the carboxyl groups of the molecules will face the metal while the methyl groups will extend outward. This does not necessarily mean that the molecules are stationary but that at any moment the majority of the carboxyls will face the metal while very few will extend outward (solid/air interface). If a droplet of water comes in contact with such a surface the carboxyl ends of the molecules are attracted by the metal and the water and there will be a change in the initial orientation of the molecules. Such a reorientation should be followed by a decrease in the contact angle of the droplet since the carboxyl groups are hydrophilic. Assuming that the decrease in the contact angle is due to reorientation of the fatty acid molecules, no such decrease should be observed if the acid molecules are firmly attached to the metal surface so that they are immobile. Such a condition can be realized if the acid molecules react chemically with the solid substrate.

A chemical bond between the metal and the acid should fix the acid molecules in stationary positions with the methyl groups extending outward. Such a surface must be hydrophobic and the contact angle should not change by allowing the droplet to age on it.

Thus, if a monolayer of fatty acid is deposited on a metal substrate and the fraction of molecules which are chemically bonded with the metal is varied at will, it should be possible to relate the contact angle to the mobile fraction of the molecules of the acid. The degree of reorientation, on the other hand, should be proportional to the mobile fraction of the monolayer. As will be seen later, this can be done by allowing a monolayer of stearic acid to react with silver at a very slow rate or by depositing mixed monolayers of fatty acid and fatty alcohol on a copper substrate.

The approach just described calls for a monolayer deposited on a metal substrate and has the purpose of providing qualitative information with regard to molecular reorientation. The next phase of the experimental program is to provide information for the case where a multilayer of fatty acid is brought in contact with water. In this case the top atomic layer of the solid surface is composed of methyl groups while the carboxyl ends of the acid molecules face the bulk of the acid and are associated with other carboxyl groups. The study of the wettability of such a surface should provide information which will test the equilibrium and kinetic considerations described earlier. The kinetic study of the reaction will include the variation of the temperature since such a study is necessary for the determination of the energy and entropy of activation.

EXPERIMENTAL APPARATUS

TROUGH

The trough from which the monolayers were deposited, was made out of Plexiglas and has the dimensions 10 x 35 inches which allows for sufficient surface for the spreading of the monolayer. The depth of the trough is only one-half inch across for 32 inches of its length. The remaining three-inch length is five inches deep. The latter allows for dipping of the slides which pick up the monolayer. Provisions have been made to prevent flooding during washing of the trough by channeling the overflowing water to the one end of the trough where it can easily be collected. The trough rests on pressboard which is supported by a tripod screw-leveling device. The dipping slides are hung from the pulley shaft which is supported by a wooden frame. The pulley is belt-connected to a variable speed motor which lowers or raises the slides. The picture in Fig. 1 shows the trough in detail. The essential parts are numbered as shown.

1. The tripod leveling device.
2. Planar pressboard where the trough rests.
3. The actual surface of the trough.
4. Floating Teflon thread for separating the monolayer from the compression oil (piston oil).
5. Paraffin-waxed glass rod for sweeping the water surface.
6. Channel for directing the overflowing water.
7. Extra depth of the trough for dipping the slides.
8. Dipping slides.

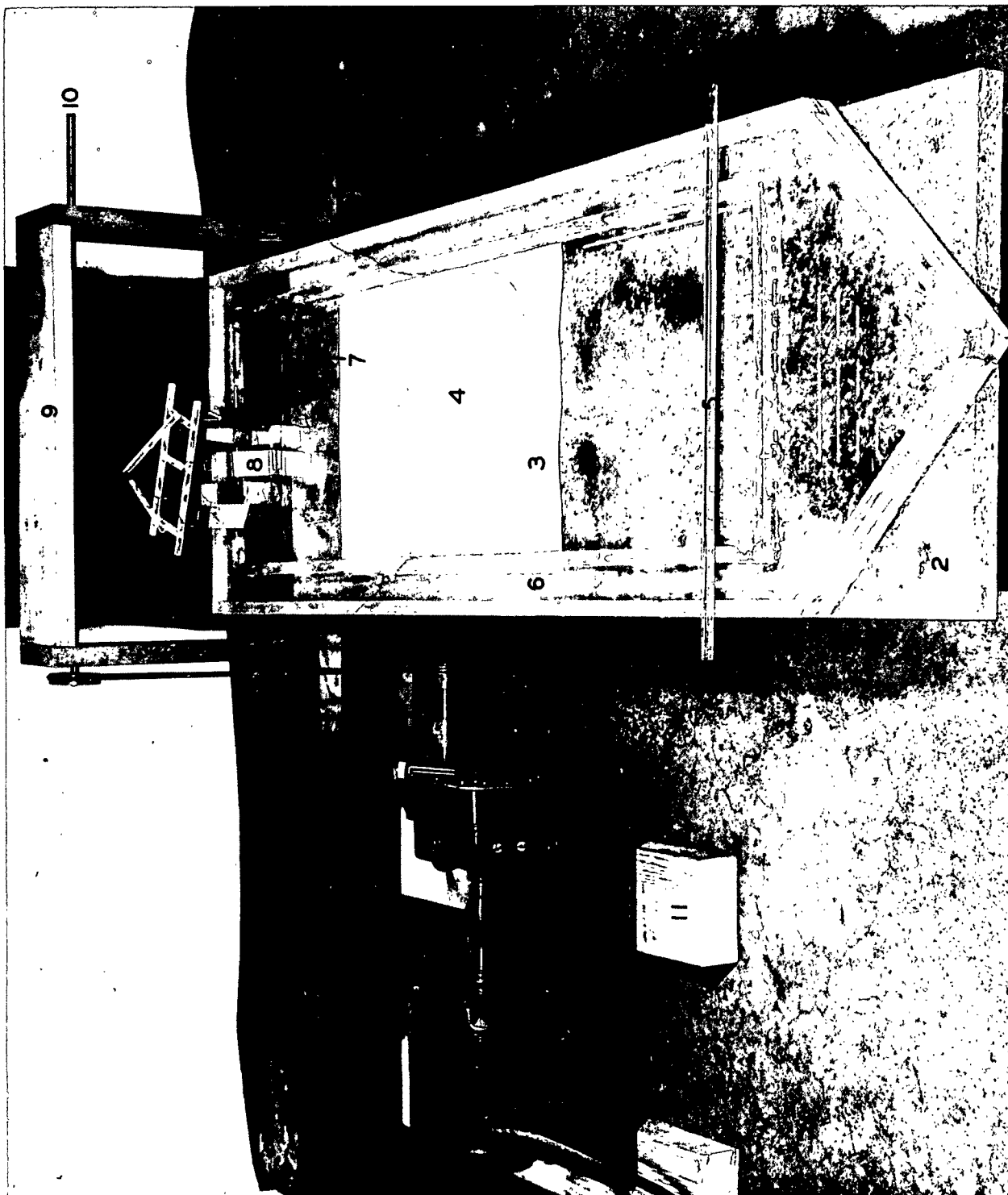


Figure 1. Apparatus for Deposition of Monolayers

9. Wooden frame for support of the pulley shaft.
10. Metal pulley shaft.
11. Variable speed motor for raising or lowering the slides.

COUNTING DEVICE

The β -radiation counting device was a G. M. tube of the plastic-window type using helium at 0°C. The gas-flow counter was connected to a Berkeley decimal scaler (Model 2000). This gas-flow counter allowed for the estimation of monolayers and multilayers deposited over an area of a one-inch circle or 5.03 cm.².

CONTACT ANGLE APPARATUS

The apparatus used for measuring the angle of contact is, essentially, the same one used by Guide (40) in which a photograph of a water droplet resting on a slide coated with the monolayer or multilayer is taken. This apparatus consists of the following essential parts and is shown pictorially in Fig. 2.

1. A 150-watt opaque incandescent lamp.
2. An infrared filter containing a 2% aqueous solution of copper sulfate.
3. A 0.6-cm. diaphragm.
4. A pipet guide.
5. Brackets which will hold the "butter dish" (transparent plastic box with plane sides) in a level position.
6. Butter dish inside which the slide is set.
7. A 48-mm. objective lens.

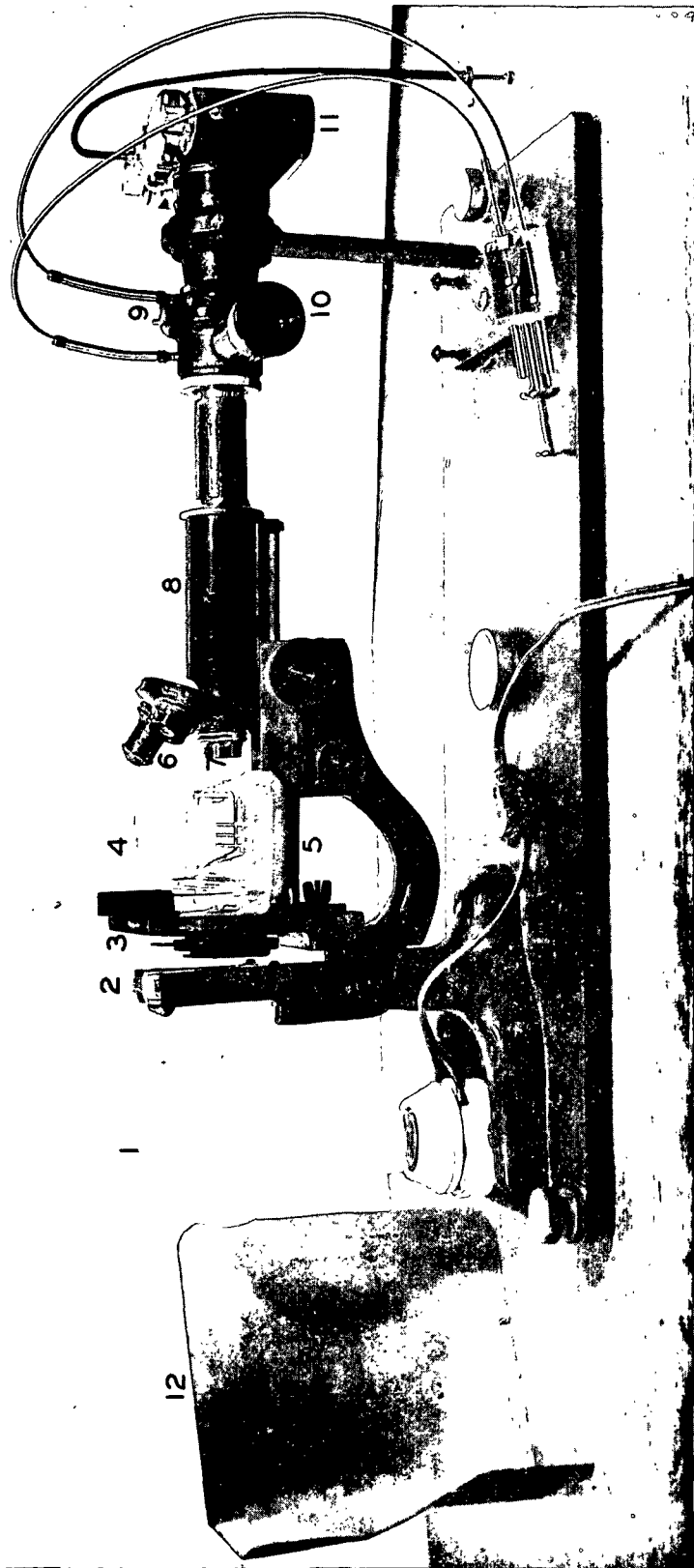


Figure 2. Apparatus for Measuring Contact Angles

8. The microscope tube, positioned in the same plane as the slide.
9. A Wetzler 1/2X adapter which replaces the normal microscope ocular. The front of this adapter fits into the microscope tube and has an eyepiece (10) extending at right angles from its main body. One can view the object through the eyepiece by means of a built-in prism. The back of this adapter is threaded to accommodate a 35-mm. Leica camera (11) whose lens system has been removed. The Wetzler adapter contains both the lens and shutter to be used with the camera body. The camera body is used merely as a film holder.
12. A metal cover for the lamp and filter.

Adox KB 14 black and white film was used throughout this work, and the shutter speed was 1/10 second. The total magnification obtained with this instrument was 15 diameters.

The only modification of the apparatus from that used by Guide (40) is that the slide is enclosed in a transparent plastic box where saturated conditions are maintained for the prevention of evaporation. The transparent plastic box allows pictures to be taken without removing the lid of the plastic box. A multitude of small spherical droplets surrounding the droplet, whose picture is to be taken, insures minimum evaporation as indicated by the constancy of the angle of contact of a water droplet on paraffin over a period of three days.

The photograph of the droplet was taken in a room where the temperature was kept constant. The slide was put inside the plastic box

and a clean 3-microliter pipet was filled with purified water by means of a microsyringe. The droplet was carefully deposited on a prefocused location of the slide and the dish was covered immediately. Pictures were taken, then, at desired intervals of aging.

The pictures were developed and the angle could be determined by simply drawing tangents on the projection of the negative or by the use of an approximate formula suggested by Back and Steenberg (41). The formula relates the contact angle with the base and the height of the droplet.

$$\tan (\theta/2) = 2h/b \quad (28)$$

where, θ = contact angle

h = height of the droplet

b = base of the droplet

✓ Drawing a tangent becomes quite difficult if the angle is obtuse and the indirect method using the above formula has quite an advantage for such angles.

Both the direct tangent method and the indirect method using the above formula were compared measuring the angles on droplets resting on paraffin layers. The results show that the indirect method gives results with a standard deviation of 0.84° as compared to 1.76° of the direct method. Therefore, the indirect method of measuring the angle of contact was used throughout this work. Appendix I shows the derivation of the above formula and the evaluation of the contact angle-measuring apparatus.

PROCEDURES AND MATERIALS

GENERAL STEPS

As should be expected, layers of fatty acid or alcohol deposited on glass slides from the melt have the disadvantage of having rough surfaces. Thick layers also have the disadvantage of being able to absorb more liquid and may not have as good orientation of the molecules as desired for reproducible results. The deposition of monolayers and multilayers on a smooth solid surface is highly desirable. The Langmuir-Blodgett technique of depositing monolayers and multilayers is quite useful for such purpose but it has the disadvantage that not all the molecules are in the free acid state but a portion of them is in the salt form since some calcium chloride is necessary for the deposition of multilayers. In other words, the water substrate upon which the stearic acid film is spread contains traces of calcium ions which help form a highly condensed film which deposits with ease. Fortunately, Sobotka, Demory, and Chanley (42) in a recent publication describe a method which allows for the deposition of pure stearic acid multilayers. The method consists of adding benzidine in the substrate instead of calcium ions. The benzidine ions give up the acid upon deposition and remain in the water instead of being deposited along with the acid. The analytical test used by Sobotka for benzidine in the deposited multilayer shows that the technique is valid. This technique was used for the deposition of multilayers throughout this work.

The deposition of monolayers must be reproducible if the results are to be meaningful. Thus, considerable time was spent to find the conditions for best deposition. The surfaces, the wettability of which is to be studied, are stearic acid monolayers and multilayers; stearic acid and stearyl alcohol mixed monolayers, and surfaces of myristic and lauric acid, respectively. ✓ Since myristic and lauric acid cannot be deposited in the form of multilayers other means for preparation of satisfactory surfaces had to be sought. Thus, the preparatory steps to be considered are:

1. Preparation of radioactive stearic acid and stearyl alcohol solutions.
2. Preparation of solid substrate.
3. Preparation of the water substrate.
4. Spreading of the film and its deposition on the solid substrate.
5. Radioactive counting.
6. Reproducibility of monolayers of stearic acid and mixed monolayers of stearic acid and stearyl alcohol.
7. Preparation of lauric and myristic acid surfaces.

PREPARATION OF RADIOACTIVE STEARIC ACID AND STEARYL ALCOHOL SOLUTIONS

Radioactive stearic acid and stearyl alcohol were purchased from Volk Radiochemical Company in 0.5 mc. and 0.1 mc. quantities. Stearic acid solutions of 0.06 and 1.64 $\mu\text{c}/\text{mg.}$ activities were prepared by mixing portions of the active substance with the required inactive acid (m.p. 69.6°C.) and dissolving in benzene in a 1:1000 ratio.

Stearyl alcohol solutions were made by mixing the active alcohol with an inactive alcohol (m.p. 58.5°C.) and inactive stearic acid. Solutions of 100, 65, 48, 32, and 0% stearyl alcohol-stearic acid were prepared. The 100% stearyl alcohol solution had an activity of 0.88 $\mu\text{c.}/\text{mg.}$

PREPARATION OF THE SOLID SUBSTRATE

The solid upon which the monolayer or multilayers are to be deposited must be absolutely smooth and clean. For this, glass slides were cleaned first with cleaning solution and finally with Alconox and distilled water. The glass slides were coated with a film (about 1000 A. thick) of metallic copper or silver by the vacuum evaporation technique. If more than a few minutes elapsed between the metallic coating and the deposition of the acid film the solid substrate was cleaned with hot benzene before being used. Organic matter is easily removed from the silver coating by hot or even cold benzene provided there is no chemical reaction involved. Copper has been chosen for the reason that the stearic acid monolayer reacts chemically with it rather rapidly while the reaction with silver is very slow.

PREPARATION OF THE WATER SUBSTRATE

The water upon which the acid film spreads must be quite clean if a pure film is to be deposited. The acid may not spread on a water surface which is contaminated with organic matter. The water used was first filtered by a Fulflo filter and then passed through a Penex M-8 resin column. This water seemed to be free of organic matter as indicated by its surface tension (72.4 dynes/cm. at 25°C.) and practically

free of inorganic ions as indicated by its specific conductance ($0.69 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at $25^{\circ}\text{C}.$).

The water was adjusted to 10^{-4} M of benzidine and $2 \times 10^{-4} \text{ M}$ of KHCO_3 with a resulting pH of 7.3. The water was poured into the waxed Plexiglas trough after the trough had been thoroughly cleaned with Alconox and distilled water. The water surface was then swept with a waxed glass rod to remove any contamination which would inhibit spreading.

SPREADING OF THE FILM AND ITS DEPOSITION ON THE SLIDES

Once the water surface was ready the slides (usually six) were hung from the pulley rod and immersed completely into the water. The water surface was again swept with the waxed rod to ensure cleanliness. The stearic acid (dissolved in benzene at 1:1000 ratio) was deposited on the clean water surface and spreading was observed by noticing the movement of the Teflon thread resting on the surface of the water. Four minutes were allowed for the evaporation of the benzene which can be seen by the indentation of thread since stearic acid molecules get closer to each other after the benzene has evaporated. At the end of the four minutes the piston oil (\checkmark oleic acid in benzene) was added on the other side of the thread (clean surface) which compresses the monolayer to a minimum area (20 \AA^2 per molecule). Four minutes were allowed again for the evaporation of the benzene from the piston oil monolayer. At the end of the four minutes the plates were allowed to rise slowly by the use of a variable speed motor. A monolayer is deposited on the solid plates during the upward trip of the

slides. Once the first layer is deposited the motor can be reversed and the slides are immersed again at the same speed; thus, another monolayer is deposited on the down trip. The procedure can be repeated many times. Once the deposition is completed the slides are removed from the pulley rod and allowed to hang in a clean place (desiccator) until used. It was thought that the speed of deposition would have an effect on the deposition of the layers. For this purpose several depositions were made at different speeds using radioactive stearic acid and copper-coated slides. The results shown in Table II indicate that very slow speeds are required for maximum deposition.

TABLE II

THE EFFECT OF SPEED OF DEPOSITION

Speed of Deposition, cm./min.	Radioactivity of Monolayer on Copper Above Background, c.p.m.
15	25
10	50
5	69
3	71
2	71

It is seen that a speed of $\sqrt{2-3}$ cm./min. is required for maximum deposition. All subsequent depositions were made with this speed.

RADIOACTIVE COUNTING

Radioactive counting provides an excellent analytical technique for monolayers. It would be practically impossible to measure monolayer quantities by any other method. The counting was done by a helium gas flow counter which allows for counting over an area of a one inch

circle or 5.03 cm.². Since the microscope slides are one inch wide all countings throughout this work were made over an area of 5.03 cm.².

The accuracy of counting depends on the activity of the sample, the total number of counts, and the time allowed for counting. Simple statistical considerations (43) show that the rate and the accuracy of counting is given by:

$$\underline{R}_X = (\underline{N}_s/\underline{t}_s - \underline{N}_b/\underline{t}_b) + (\underline{N}_s/\underline{t}_s)^2 + \underline{N}_b/\underline{t}_b)^{1/2} \quad (29)$$

where, \underline{R}_X = rate of counting in counts per minute, c.p.m.

\underline{N}_s = total number of counts of the sample over time \underline{t}

\underline{N}_b = total number of counts of the background over time \underline{t}_b

Thus, simple calculations allow the determination of the time of counting or the total number of counts required for a certain accuracy.

Thus, for a sample with about 1200 c.p.m. above background the accuracy will be ± 5 c.p.m. if a total of 5000 counts are taken. It is seen that low activity samples take a longer time for the same accuracy. The above mentioned ± 5 c.p.m. accuracy was used throughout this work unless otherwise stated.

REPRODUCIBILITY OF MONOLAYERS

It is important that monolayers can be reproducible during a single run and different runs. Tables XII-XVI of Appendix II show results indicating the reproducibility as measured by radioactive counting, of stearic acid, stearyl alcohol, and mixed monolayers on different solid substrates. The results show that such monolayers can be reproduced with 7% variation or less. Tables XVII and XVIII of the same

Appendix show the degree of desorption of the different monolayers in benzene and water. Such desorption studies are important because they reveal the degree of spreading or solubility of the monolayers from the solid substrates. It is seen that the monolayers are quite stable and cannot be removed by water from the solid substrate unless drastic means such as high temperatures are applied. Benzene will dissolve the monolayers provided there is no chemical reaction involved between the monolayer and the solid substrate.

The data of Appendix II show the following important information with regard to deposition, reproducibility, and stability of the monolayers.

1. Reproducibility of monolayer deposition within a run and between runs can be attained with 7% error or less.
2. The radioactive counts per minute depend on the type of substrate used since different substrates have different backscattering coefficients.
3. Monolayers can be deposited with ease from pure water but multilayers require some cations to be present.
4. Multilayers of stearic acid can be deposited by Sobotka's benzidine method with good reproducibility.
5. Multilayers of stearic acid cannot be deposited from pure water with any reasonable accuracy. Stearyl alcohol multilayers cannot be deposited by the Langmuir technique.
6. Mixed monolayers of stearic acid and stearyl alcohol can be deposited on copper and silver substrates using oleic acid as piston oil.

7. Monolayers of stearic acid on silver and glass, aged up to 48 hours after deposition, can be desorbed with cold benzene. Corresponding monolayers on copper cannot be desorbed. Stearyl alcohol monolayers can be desorbed with cold benzene from all three substrates.
8. Stearic acid monolayers on glass do not appreciably desorb with water at 25°C. but the desorption becomes significant at higher temperatures.

PREPARATION OF LAURIC AND MYRISTIC ACID SURFACES

Deposition of multilayers of lauric and myristic acids at room temperature by the Langmuir-Blodgett technique is not satisfactory possibly due to shorter chain length which would keep the monolayer from becoming condensed. Thus, if the wettability of these acids was to be studied some satisfactory way of preparing the surface had to be found.

The lauric and myristic acids used had melting points of 43.6 and 53.2°C., respectively. Each acid was dissolved in benzene at 1:1000 ratio and 0.5 ml. of each benzene solution was slowly deposited over an area of one square inch of a glass slide coated with metallic silver as formed by the vacuum evaporation technique. This gives a surface which would consist of about four hundred molecular layers if uniform distribution of the molecules were possible. After the benzene evaporated, the slide was heated in an oven for a few minutes at a temperature of 55°C. This melts the acid and distributes it uniformly over the solid. The slide was removed from the oven and allowed to

stand in a desiccator overnight before any wettability studies were carried out. The type of surface just described is equivalent to that formed by drawing the slide from the melted acid but the present technique is suitable when small amounts of pure acids are available. The roughness of this surface was apparently minimized.

EXPERIMENTAL RESULTS

THE WETTABILITY OF STEARIC ACID AND PARAFFIN SOLIDIFIED IN THE PRESENCE OF AIR AND WATER

The wettability of stearic acid solidified in the presence of water and air was first studied by Nietz (24). A new feature of this experiment, however, is its parallel comparison with paraffin solidified in contact with water and air.

The essence of the experiment consists of melting the stearic acid or the paraffin in hot water (the acid and the paraffin wax float on water) and allowing the system to cool. Thus, one side of the solid disk is solid surface formed in contact with air and the other is solid surface formed in contact with water. The surfaces formed in the above manner are quite rough since the solids are quite crystalline; the surface towards the water seems to be rougher than the surface towards the air. The roughness decreased when the system was cooled quite rapidly.

Once the temperature of the system was in equilibrium with the room temperature (23°C.) the solid was separated from the water and allowed to stand over CaCl_2 for 10 minutes. The wettability of both surfaces was tested by measuring the angle of contact at the end of the 10 minutes. Each water droplet was allowed to age 20 seconds before a picture was taken. The results obtained are shown in Table III.

TABLE III

THE CONTACT ANGLE OF WATER ON AIR AND
WATER-FORMED SURFACES AT 23°C.

	Stearic Acid	Paraffin
Air surface	126	121
Water surface	57	113

The contact angles given here are averages of five measurements and the scatter did not exceed 5°. The results show that the water surface of the stearic acid is much more wettable than its air surface, while both surfaces of paraffin show about the same wettability. The results have only qualitative meaning since the surfaces formed in the above manner are quite rough.

The increased wettability of the stearic acid surface crystallized in contact with water can be understood if the assumption is made that the water-formed surface contained an appreciable number of carboxyl groups. The orientation, however, cannot be considered to be complete in view of the finite contact angle. It is also possible that the orientation was complete but a portion of the outer molecular layer remained on the water upon separating the solid from the water.

AGING OF HYDROPHOBIC SOLIDS OVER WATER AND THE WETTABILITY OF THE SOLIDS

Fox and Zisman (12) have stated that the angle of contact of the higher boiling liquids on the low energy surfaces are the same in air as in air saturated with vapor. It was thought, however, that aging of the solids in moist atmosphere may change the wettability of the

solids. For this, layers of paraffin, stearic acid, and stearyl alcohol were deposited on glass slides from the melt, and their wettabilities were tested after the slides were allowed to stand over water in a desiccator for various time intervals. Contact angle measurements were made after the droplet had been deposited for 20 seconds. The results are summarized in Table IV.

TABLE IV
THE CONTACT ANGLE OF WATER ON SURFACES
CONDITIONED OVER WATER AT 23°C.

Aging Time, hours	Paraffin	Stearic Acid	Stearyl Alcohol
0	115	128	124
10	115	127	123
25	114	126	122
50	114	125	120
75	114	125	119

The results indicate that the change in wettability with aging over water is not appreciable. It seems that very little water vapor is adsorbed by the hydrophobic layers. This can be understood by the fact that the concentration of water molecules at the solid surface at any moment is quite small; the mobility of the polar molecules of the acid and the alcohol is also quite small and very few hydrophilic groups are at the surface to attract any water molecules.

The contact angles are rather high for the surfaces formed in the above manner. This could easily be due to the roughness of the surfaces.

THE WETTABILITY OF STEARIC ACID AND STEARIC ACID-STEARYL
ALCOHOL MIXED MONOLAYERS ON COPPER AND SILVER SUBSTRATES

As mentioned earlier it is desirable to deposit a monolayer on a substrate and vary the number of molecules which are mobile. This would allow for the preparation of a surface having the same total number of molecules of fatty acid but different amounts capable of any movement or reorientation. Thus, the wettability of such a surface should increase when the mobile fraction of the monolayer increases.

Two methods were used for preparing surfaces with variable mobile fractions of molecular monolayers. Both depend on the reactivity of the monolayer with the solid substrate. It was found that a monolayer of stearic acid deposited on a copper¹ surface became quite immobile very quickly but a monolayer of the same acid deposited on a silver surface became immobile very slowly. The mobility of the monolayer was tested by the degree of solubility in benzene at room temperature. It is thought that the acid is chemically bonded with the substrate thus becoming immobile. It was also found that stearyl alcohol deposited on either copper or silver was mobile and could easily be removed with benzene. The desired surfaces, then, could be prepared by either depositing a mixed stearic acid-stearyl alcohol monolayer on copper or by depositing a stearic acid monolayer on silver and allowing it to age for different time intervals.

✓ Mixed stearic acid and stearyl alcohol monolayers of variable composition were deposited by the Langmuir technique on copper and silver

¹ Reaction of stearic acid and copper substrate has also been reported by Beischer (44).

slides formed by the vacuum evaporation technique. The deposited monolayers were allowed to stand over calcium chloride in a desiccator for 48 hours. This is sufficient time to ensure complete reaction of stearic acid and copper, while the reactivity between the stearyl alcohol and copper and that of stearic acid and stearyl alcohol with silver is negligible. After this aging process the wettability of the surfaces was tested by photographing a droplet in the manner described earlier. Equilibrium between the droplet and the surface was reached within five minutes. The equilibrium contact angles for the different monolayers are shown in Table V. It is seen from this table that for copper substrate the contact angle decreases with increase in the stearyl alcohol content of the monolayer but for silver substrate the contact angle is practically unchanged. These results seem to be in accordance with the argument that the copper will react with stearic acid and anchor the acid molecules in stationary positions. The reactivity of stearic acid and silver aged for 48 hours seems to be insignificant.

It was thought that the stearyl alcohol may spread over the water droplet and reduce the surface tension of the water which in turn would change the contact angle. To test this, the copper-substrate monolayers were dipped in water for five minutes after which they were withdrawn and the radioactivity was counted. Withdrawing of the slides was done in such a manner that no redeposition of fatty acid or fatty alcohol from the water surface was possible. The loss in radioactivity was too small to be significant as shown by comparing columns two and three of Table V. Thus, the decrease in contact angle cannot be due to spreading. The results can be explained satisfactorily by the molecular reorientation

TABLE V
CONTACT ANGLES OF WATER ON MIXED MONOLAYERS OF
STEARIC ACID AND STEARYL ALCOHOL AT 23°C.

Stearyl Alcohol, %	Copper Slides		Equilibrium Contact Angle, θ_E	
	Radioactive Count ^a Before Dipping in Water, c.p.m.	Radioactivity After Dipping in Water, c.p.m.	Monolayer on Copper	Monolayer on Silver
0	--	201	104	74
31.6	210	201	93	73
48.0	300	286	88	72
65.0	415	392	84	72
100.0	651	610	71	70

^a The radioactive count is proportional to the amount of stearyl alcohol present in the mixed monolayer on copper.

of the alcohol molecules in the copper substrate and both the acid and alcohol in the silver substrate.

If a stearic acid monolayer, deposited on a silver substrate, is allowed to age for a long time it is found that benzene does not remove the monolayer at room temperature. This indicates that the stearic acid becomes immobile or it reacts with the solid substrate just like it does with the copper substrate but the time of reaction is much longer. Thus, by simply aging such a monolayer one can prepare a surface with variable portions of molecules which are capable of mobility. For this, stearic acid monolayers were deposited on silver-coated slides and allowed to age over water for as long as forty-three days. Over this period the monolayers were tested for wettability and chemical reaction of the

stearic acid. The wettability was measured by determining the contact angle of a water droplet on the coated slide. Equilibrium seemed to be reached within five minutes. The amount of immobile stearic acid was measured by determining the amount of stearic acid dissolved in benzene (dipping the slide in benzene for two minutes¹). This was done by taking the radioactive count of the slide before and after the benzene treatment. Table VI shows the results obtained.

TABLE VI

REACTION OF STEARIC ACID AND SILVER SUBSTRATE AND
THE WETTABILITY OF SUCH SURFACE AT 23°C.

Sample No.	Time of Aging Over Water, days	Count Before Dipping Into Benzene, c.p.m.	Count After Dipping Into Benzene, c.p.m.	Reaction, %	Equilibrium Contact Angle, θ_E
1	0	1210	125	10.3	73
2	10	1288	497	38.5	85
3	10 ^a	1320	346	26.2	78
4	13	1447	943	58.0	90
5	32	1280	1056	82.5	99
6	43	1183	1143	96.6	105

^a Aged over calcium chloride.

It is seen that the rate of reaction is quite slow and approaches completion after forty-three days. The equilibrium contact angle for each level of aging is in accordance with the degree of mobility of the monolayer. Initially, the surface is hydrophobic but since there is molecular mobility in the monolayer the contact angle drops to 73° within

It was found that two minutes was sufficient time to remove the mobile portion of the monolayer.

five minutes. When the slide is aged for forty-three days the molecular mobility is depressed (due to chemical reaction with the solid) and the contact angle remains high or 105° . The results can be understood if molecular reorientation is assumed. The carboxyl ends of the stearic acid gradually turn towards the water and increase the wettability of the surface. When the stearic acid molecules are not capable of such mobility the wettability of the surface remains practically constant.

THE WETTABILITY OF STEARIC ACID MULTILAYERS

The purpose of this experiment was to study the wettability of stearic acid multilayers deposited on silver-coated slides and any change in wettability that may occur due to prolonged interfacial aging. This surface, due to the method of preparation, is a surface of minimum roughness, minimum number of molecular holes, and maximum molecular orientation.

The experiment was carried out by depositing seven monolayers of stearic acid on a silver-coated glass slide by the Langmuir-Blodgett technique using benzidine as the dissolved cation in the water. The slide was allowed to stand over calcium chloride in a desiccator for at least 24 hours to ensure removal of possible moisture on the stearic acid surface and any other changes that may occur in the thin multilayer film. The slide was then set in the contact angle apparatus and the angle change of a small spherical droplet with interfacial aging was followed by taking pictures of the droplet at different time intervals. This method of measuring the contact angle has the disadvantage of varying the interfacial area of stearic acid and water since the area

will slightly increase upon increasing the wettability of the surface. Although such a change was quite small for the present work it was thought that the results should be checked in some other way. Aging the slide by simply dipping it into water may cause partial loss of the monolayer since a rather large quantity of water will be used; but aging a portion of the slide by a rather large drop of water seemed to be desirable. Thus, a large drop of water was deposited on the slide which, after the aging time interval, could be removed completely by a pipet and the wettability could be tested by photographing a newly deposited droplet on the conditioned surface. The wettability of a paraffin layer on a glass slide, deposited from the melt, was studied in parallel with that of stearic acid. The roughness of the layer was minimized by adjusting the rate of cooling of the layer. The results are presented in Table VII and Fig. 3. Each point or number represents an individual measurement. It is seen that the contact angle of water on stearic acid is gradually decreasing over a period of a few hours while that of paraffin remains practically unchanged. It is also seen that the two ways of conditioning the surface with water give identical results.

Since the equilibrium value is not quite sharp it was thought that maybe after a certain point the change was quite slow and never actually terminated. To test this idea, slides of stearic acid multilayers were conditioned with water for ten days and their wettabilities were tested in the usual manner. The results are shown in Table VIII and indicate that equilibrium is reached at about 69° contact angle which is close to 71° shown in Fig. 3.

TABLE VII

THE WETTABILITY OF STEARIC ACID AND PARAFFIN AT 23°C.

Interfacial Aging, hours	S T E A R I C A C I D		P A R A F F I N	
	Contact Angle by Allowing the Droplet to Age	Contact Angle After Aging Por- tion of the Slide by a Large Drop	Contact Angle by Allowing the Droplet to Age	Contact Angle After Aging Por- tion of the Slide by a Large Drop
0	104.0	103.8	108.0	107.1
1	100.0	98.3	--	--
2	95.0	94.9	107.5	106.3
4	87.5	87.5	--	--
6	82.0	81.6	106.0	105.9
8	76.0	75.7	--	--
10	74.5	73.0	105.5	104.0
14	72.5	72.0	--	--
23	71.5	70.6	103.5	103.1

TABLE VIII

CONTACT ANGLE OF STEARIC ACID
CONDITIONED WITH WATER AT 23°C. FOR 10 DAYS

Slide no.	1	2	3	4
	70	71	65	72
	68	69	66	73
	69	70	68	69
	—	—	—	—
Mean	68	70	67	71

Grand average = 69.2°

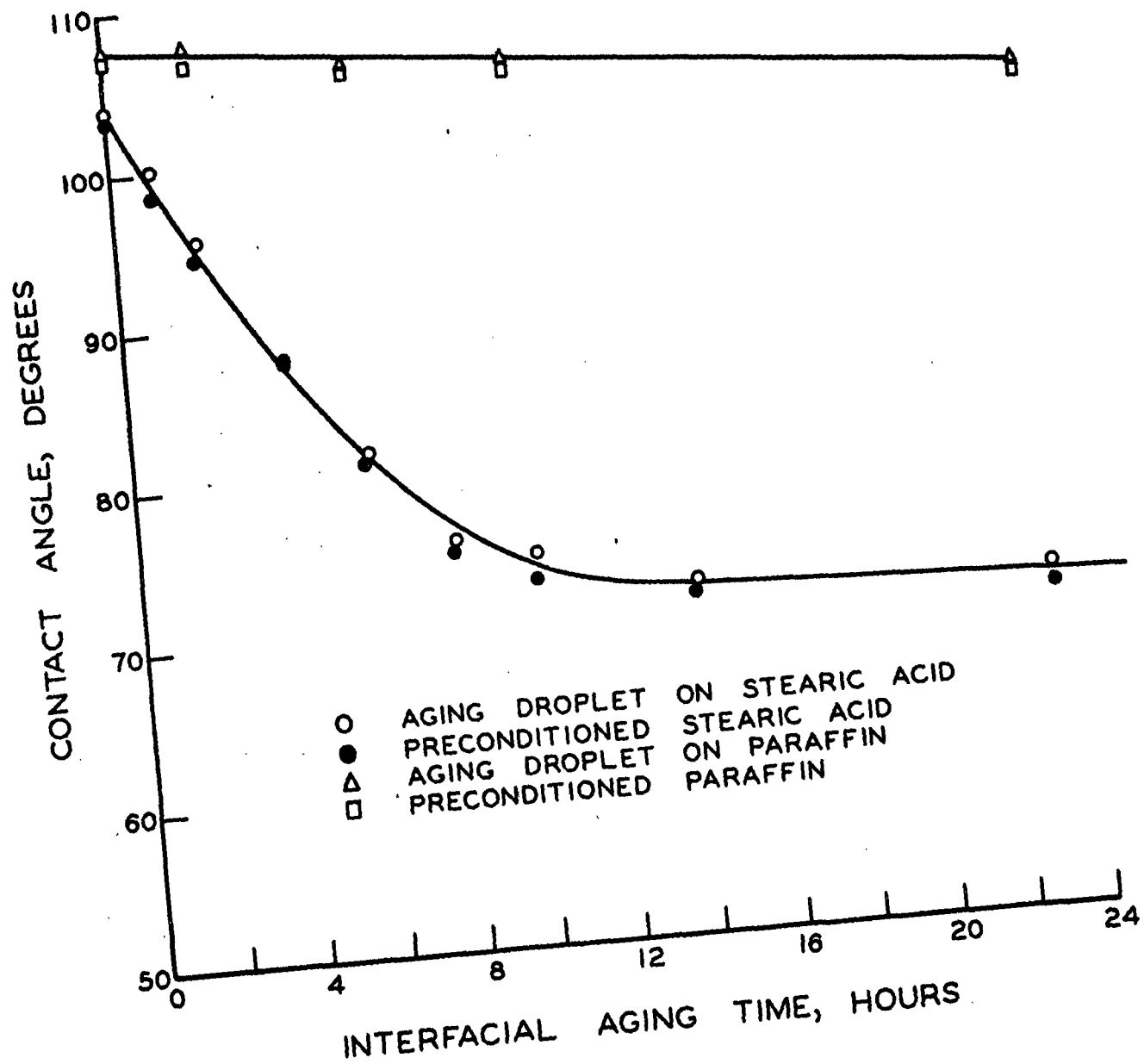


Figure 3. The Effect of Aging on the Wettability of Paraffin and Stearic Acid at 23°C.

THE EFFECT OF TEMPERATURE ON THE RATE
OF WETTING OF STEARIC ACID MULTILAYERS

The previous experiment showed that the change in the contact angle of multilayers of stearic acid with prolonged interfacial aging in water is quite large. The wettability of paraffin, on the other hand, is practically unchanged with prolonged interfacial aging. It is the purpose of the present experiment to extend the study of wettability of stearic acid multilayers to other temperatures. This will provide information necessary for further understanding of the kinetics of the reaction.

The range of temperatures studied is limited in view of experimental difficulties encountered at high and low temperatures. The surface tension of the water and the solid are functions of temperature. In addition, higher temperature presents evaporation and condensation difficulties which would make contact angle measurements unreliable. Consequently, temperatures over 35°C. were not considered.

The experimental work consisted of the time study of the contact angle of a water droplet on a multilayer surface of stearic acid at different temperatures. The temperature was controlled by carrying out the experiment in a variable temperature room where the temperature could be controlled within half a degree (°C.) or less. Ample time was allowed for all equipment and materials used to reach thermal equilibrium before any experiment was started.

The results obtained are tabulated in Table IX and are shown graphically in Fig. 4 and 5. It is seen that the effect of temperature

TABLE IX
THE EFFECT OF AGING ON THE WETTABILITY OF STEARIC ACID
MULTILAYERS AT DIFFERENT TEMPERATURES

Time of Aging, hours	Contact Angle, °					Time of Aging, min.	30.0°C.	35.0°C.
	13.5°C.	15.5°C.	25.0°C.	28.5°C.				
0	105.0	105.0	104.0	104.5	0.3	92.5	89.0	
0.5	--	--	--	97.5	1	89.5	77.5	
1	--	--	96.6	91.4	2	76.0	65.0	
2	--	--	92.2	83.8	3	70.0	--	
3	--	--	--	78.5	4	67.5	60.0	
4	--	--	84.4	74.6	6	62.5	50.5	
5	98.6	96.5	--	--	8	--	44.5	
6	--	--	79.0	--	10	55.0	39.0	
8	--	--	76.1	--	12	49.5	36.0	
10	93.4	90.2	73.5	70.5	14	--	--	
14	--	--	--	--				
15	89.2	85.4	73.0	69.2				
20	--	81.6						
23	--	--						
25	82.2	78.6						
35	77.4	74.2						
45	75.0	--						
55	73.0	72.3						

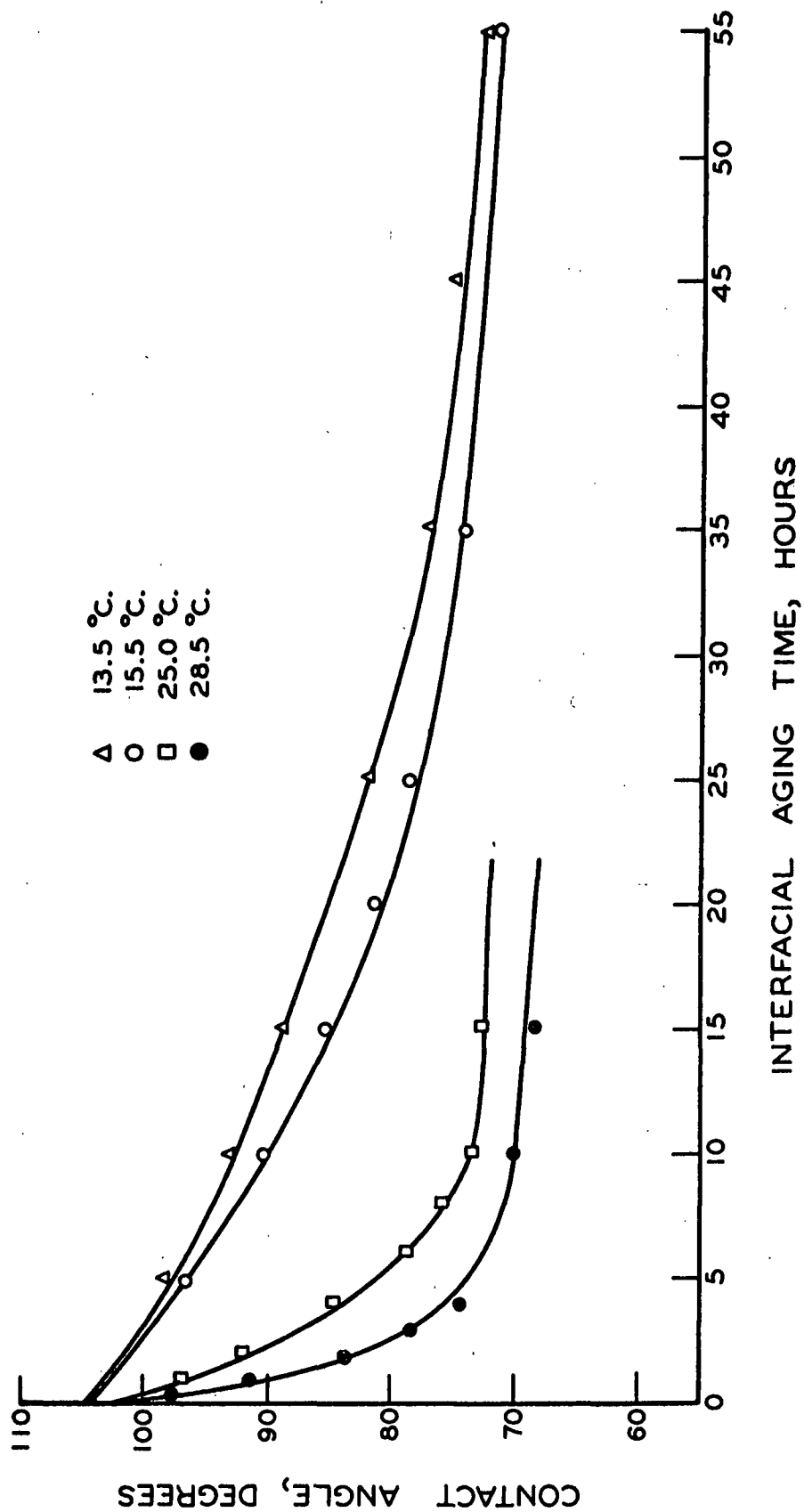


Figure 4. The Effect of Aging on the Wettability of Stearic Acid at Different Temperatures

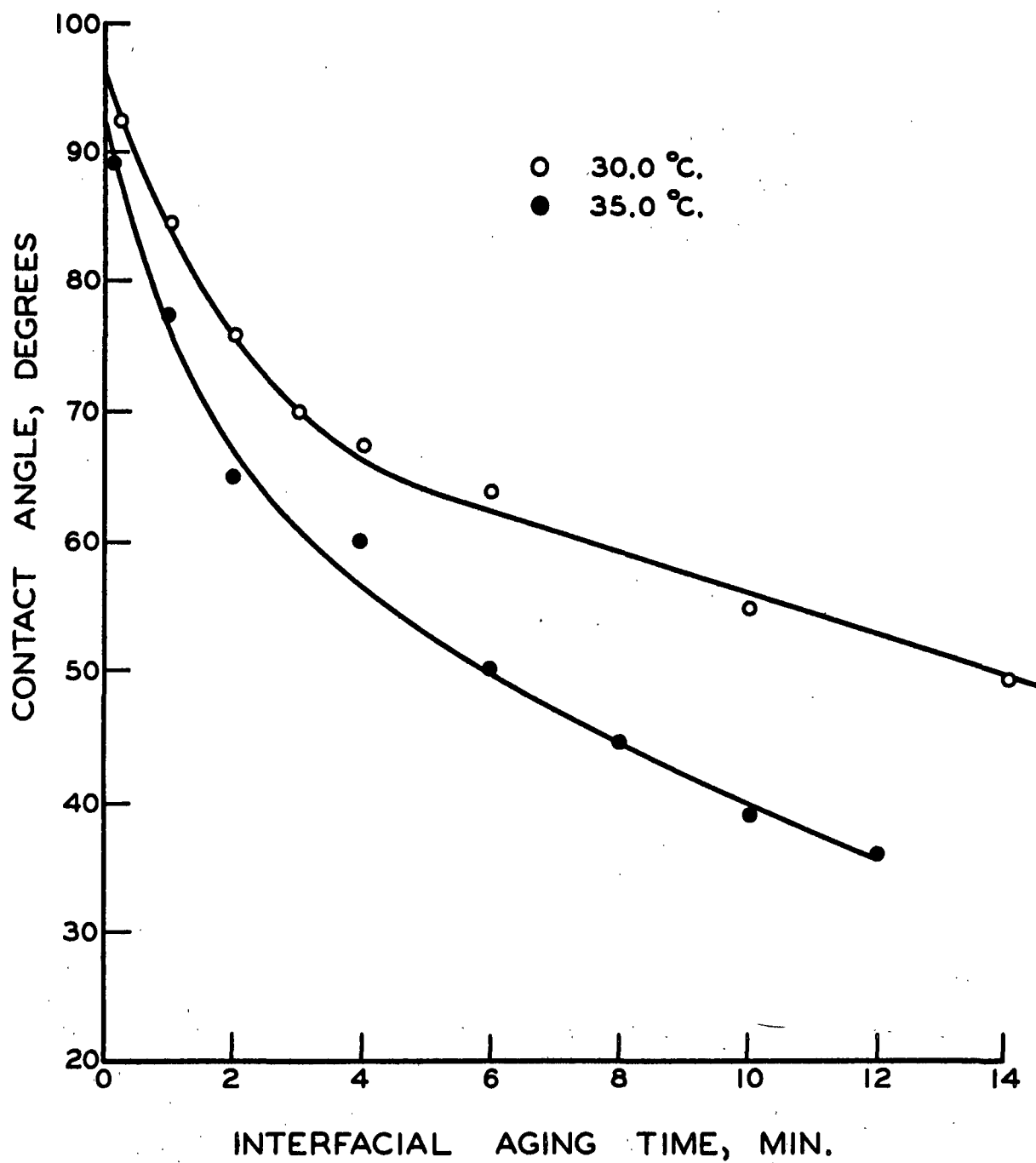


Figure 5. The Effect of Aging on the Wettability of Stearic Acid at Different Temperatures

is appreciable. It is seen also that for the temperature range 13.5-28.5°C. the reaction is normal, having a rather definite equilibrium angle of about 70° for all five temperatures considered. The results obtained at 30 and 35°C. show that the rate of reaction changes very rapidly between 28.5 and 30°C. indicating some drastic change in the system. It is possible that a transition of the surface takes place which would allow the molecules of the surface to move rather freely. The fact that the contact angle decreases below 70°, which seems to be the equilibrium contact angle for the other temperatures, is an indication that solid spreads on the water droplet thus reducing its surface tension and consequently the contact angle. The sudden change in the rate of reaction cannot be fully interpreted at the present time but it has been shown that monolayers of fatty acids on water have transition states at rather low temperatures. Adam (45) studied the effect of temperature upon the molecular area in a palmitic acid film on water under a low compressive force (1.4 dynes per cm.) and found that the molecular area almost doubled when the temperature was raised from 20 to 30°C. He attributed this sudden change to a change of state in the condensed monolayer. Beischer (44) who discusses melting phenomena of deposited monolayers claims that the two dimensional lattice of a stearic acid monolayer becomes unstable well below the normal melting point of the stearic acid in bulk (70°C.). He further states that radioautographic techniques have shown that the homogeneity of a stearic acid monolayer on mica was greatly disturbed when the monolayer was exposed to a temperature of 40°C. for three minutes. It is conceivable, then, that the surface molecular layer of stearic acid melts at a temperature as low as 30°C. In view of this abnormality in the data, it is suggested that

only data obtained below 30°C . should be treated from the kinetic and equilibrium points of view for the reaction. ---

THE WETTABILITY OF LAURIC AND MYRISTIC ACID LAYERS

The purpose of this experiment was to study the effects of chain length on the wettability of the fatty acids. The stearic acid, already discussed, has 18 carbon atoms in its molecule while myristic and lauric acid have 14 and 12 carbon atoms, respectively.

The surfaces of these acids, unlike the stearic acid surface, were prepared by depositing the benzene solution of each acid on the silver-coated slide and allowing time for the benzene to evaporate. The amount of acid in the benzene solution was such that the film would be many molecules thick. After the benzene had evaporated the slides were heated in an oven to 55°C . so that the molecules would distribute over the surface. The slides were allowed to stand over calcium chloride overnight and then they were tested for wettability in the usual manner. The results are shown both in Table X and Fig. 6. It is seen that the contact angle decreases rather rapidly for myristic acid reaching equilibrium at 70° in about 500 seconds while the contact angle of lauric acid decreases very rapidly reaching equilibrium at 69° within 10 seconds. The significant thing to notice is that both acids show about the same contact angle at equilibrium but they differ in the rate at which they reach equilibrium. It will be recalled that stearic acid had about the same equilibrium contact angle but the time to reach that value was quite long. Thus, the three acids considered show the same equilibrium contact angle. It is interesting to compare this finding with the general statement made by

TABLE X

THE EFFECT OF AGING ON THE WETTABILITY OF
MYRISTIC AND LAURIC ACID AT 25°C.

	C o n t a c t A n g l e s		
	Myristic Acid		Lauric Acid
Interfacial Aging, sec.	Run No. 1	Run No. 2	
5	--	--	73.5
10	--	--	69.0
20	101.5	--	69.0
25	--	100.0	--
50	97	--	--
75	--	94.5	--
100	90.5	--	69
150	--	84.0	--
200	81.0	--	--
250	--	78.5	--
300	73.5	--	69
350	--	73.5	--
400	72.0	--	--
450	--	72.0	--
500	70.5	--	--
600	70.0	69.5	--

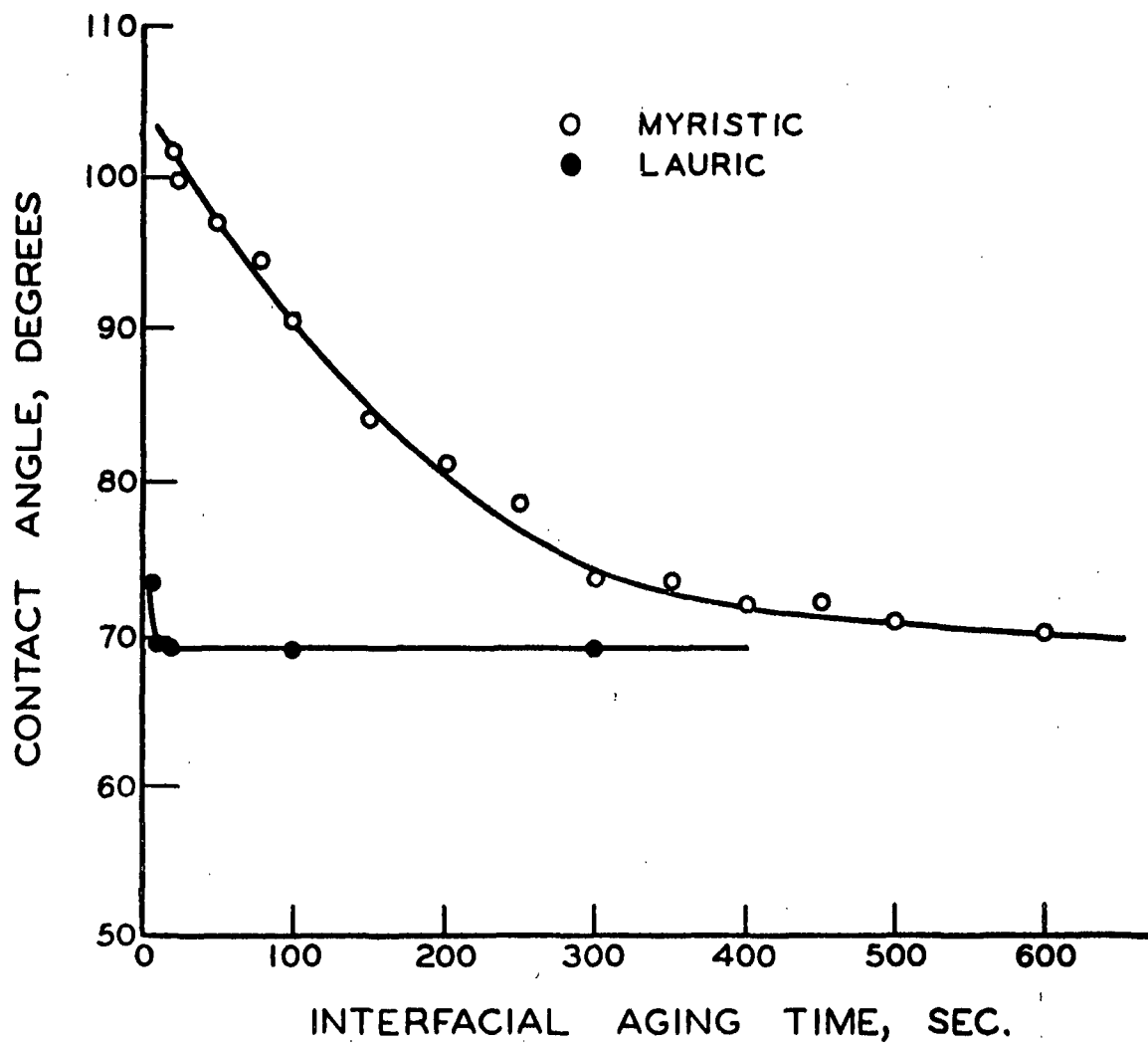


Figure 6. The Effect of Aging on the Wettability of Myristic and Lauric Acid at 25°C.

✓ Adam (1) and Harkins (34) that the adhesion between water and a liquid fatty acid is practically independent of the size of the acid molecules. One may interpret this observation by assuming that the adhesion between water and a solid fatty acid at equilibrium is the same as the adhesion of water and a liquid fatty acid but the difference lies in the time required to reach equilibrium. ✓ In the case of liquids, equilibrium is established rather rapidly owing to the mobility of the molecules in the liquid state.

SUMMARY OF EXPERIMENTAL OBSERVATIONS

The experimental observations presented above can be summarized as follows:

1. Stearic acid solidified in the presence of water gives a surface which is much more wettable than the surface crystallized in contact with air. Paraffin surfaces give, essentially, the same wettability whether crystallized in the presence of water or air.
2. Aging of hydrophobic surfaces of paraffin, stearic acid, and stearyl alcohol in water vapor does not alter the wettability of the surface.
3. The wettability of stearic acid-stearyl alcohol mixed monolayers on a copper substrate increases upon increasing the stearyl alcohol content of the monolayer. The wettability of the same mixed monolayers, however, on silver substrate is practically unchanged provided the monolayer has not been allowed to stand (age) for more than 48 hours.

4. The wettability of stearic acid monolayers on silver substrate decreases if the monolayer is allowed to stand (age) for many days. After considerable aging such a surface becomes very hydrophobic.
5. The wettability of stearic acid, myristic acid, and lauric acid surfaces increases with the solid-water interfacial aging. At equilibrium the wettability of all three acids is about the same. The rate of wetting for stearic acid increases with increasing temperature showing an unexpected increase at about 30°C.

DISCUSSION OF RESULTS

THREE POSSIBLE EFFECTS

Until now the experimental observations have been reported as such and briefly explained by the hypothesis of molecular reorientation without discussing any other possible reasons. The over-all experimental observation is that polar-nonpolar substances, like fatty acids, have low initial wettability but their wettability increases upon prolonged interfacial aging. The wettability of paraffin and fixed monolayers on the other hand, is not significantly changed with interfacial aging. It is the purpose of this section to discuss possible reasons for the observed phenomena.

Assuming purity of the systems so that only two components are involved, one would expect the change in contact angle to be the result of changes in the surface tension of the water, of the solid, and of the interfacial tension of the two components. This is obvious from the Young equation, $\cos \theta = (\gamma_{SA} - \gamma_{SL})/\gamma_{LA}$, the validity of which was discussed earlier. The changes can come about via the molecular mobility of either component or both. The water molecules can move and be adsorbed on the solid, increasing the surface energy of the solid; the solid molecules can move and spread on the water surface reducing the surface energy of the water; and the solid molecules can move so that different ends of the solid molecules are in contact with the water. The latter has been called molecular reorientation of the solid molecules. Thus, the three possible effects to be discussed in some detail are:

1. Moisture adsorption on the solid surface.
2. Spreading of the solid on the water surface.
3. Molecular reorientation at the solid surface.

THE EFFECT OF MOISTURE ADSORPTION

The effect of moisture on the contact angle is mentioned quite often in connection with the phenomenon of hysteresis. If moisture adsorbs on the solid surface it will increase the surface energy of the hydrophobic solid and the contact angle will decrease. Cassie (46) suggests that moisture cannot be adsorbed on a solid as a continuous film but only in the form of distinct clusters. A continuous film of moisture would not give a finite contact angle. He suggests that the observed contact angle is a composite of the angle which the water makes with the moisture clusters and the angle which the water makes with the hydrophobic surface not covered by moisture clusters. The contact angle of water on the surface covered with the moisture clusters is expected to be zero. This analysis can explain the hysteresis phenomenon of certain systems but the theory is not complete in view of the fact that the hysteresis can be intensified by roughness and other factors. Langmuir (27) has attributed one type of hysteresis to molecular reorientation.

It cannot be denied that if moisture is adsorbed on the surface it will decrease the contact angle. The adsorption, however, may not be appreciable for surfaces which are strongly water repellent. Moisture adsorption is not anticipated for a low energy surface since moisture would tend to increase the surface energy of the surface. The experimental

results of this investigation suggest that the moisture adsorption is negligible. The experiment on the effect of aging of hydrophobic surfaces over water shows that moisture as found in saturated air does not affect the contact angle. The data on the wettability of paraffin show that liquid water does not appreciably alter its hydrophobic nature. This indicates that moisture is not adsorbed on paraffinic surfaces. One may argue that fatty acids are not totally paraffinic but they have hydrophilic carboxyl groups at the end of each molecular chain. While this is true, it is known that the carboxyl groups are buried in the solid and are too far away from the surface to have any effect on the wettability of the surface. In the case of stearic acid they are some 25 Å. away. It will be recalled that the wetting forces are short-range forces.

It will be observed that the rates at which equilibrium is established for the three fatty acids vary at least tenfold. It cannot be conceived that the moisture would be adsorbed or absorbed at such different rates for substances of similar chemical and physical constitution. The change in contact angle with interfacial aging must be related to the molecular mobility of the solid molecules rather than that of the water. The decrease in the wettability of stearic acid monolayers which have been allowed to age for many days is further proof that the decrease in contact angle is related to the mobility of the molecules of the solid rather than the molecules of the water.

THE EFFECT OF SPREADING OF THE SOLID MOLECULES ON WATER

Spreading of the solid molecules on the surface of the water will reduce the surface tension of the water. Rideal (21) points out that

the surface pressure of stearic acid on water at room temperature is quite small to account for significant reduction in the surface tension. Furthermore, the equation $\cos \theta = (\gamma_{SA} - \gamma_{SL})/\gamma_{LA}$ shows that a change in the value of γ_L cannot account for a change in the sign of $\cos \theta$. Thus, the change in the sign of $\cos \theta$ is due to the change in the quantity $\gamma_{SA} - \gamma_{SL}$ and specifically to the interfacial tension γ_{SL} .

Assuming $\gamma_{SA} = \gamma_{CH_3} = 33.4$ dyne/cm., $\gamma_{LA} = \gamma_{H_2O} = 72.6$ dyne/cm. and a contact angle of 105° as the initial contact angle one calculates $\gamma_{SL} = \gamma_{SA} - \gamma_L \cos \theta = 52.2$ dyne/cm. This is in agreement with the interfacial tension measured experimentally for water-hydrocarbon systems (14) which is about 50 dyne/cm. Similar calculations using the equilibrium contact angle 70° , keeping γ_{SA} and γ_{LA} constant, gives an interfacial tension of 10 dyne/cm. which corresponds to a work of adhesion of 96 erg/cm.^2 which is close to the energy of adhesion for heptylic acid (a liquid fatty acid) with water (34) as well as for other fatty acids and alcohols. The results of these calculations are approximate values for the initial and equilibrium interfacial tensions of water and fatty acids. It seems that at equilibrium the adhesion of water on a solid acid surface is the same as the adhesion of water on a liquid acid surface. This indicates that the quantity γ_{SL} is the main quantity which undergoes change upon interfacial aging.

The experiment with mixed monolayers on copper where the monolayer was dipped in water and there was no loss in the radioactive count shows that little or no spreading takes place. The stability of stearic acid monolayer on glass while in water (Table XVIII, Appendix II) at ordinary

temperatures is further proof that spreading is negligible. The fact that the contact angle of the aged droplet on stearic acid multilayers is the same as the contact angle of a newly deposited droplet on the preconditioned surface (Tables VII and VIII, page 62) confirms that no significant spreading is taking place.

MOLECULAR REORIENTATION AT THE SOLID SURFACE

Since the moisture adsorption and spreading of the solid have been eliminated as the predominant causes for increase in the wettability of the fatty acids with interfacial aging it remains to consider the third possibility or the molecular reorientation at the solid surface. The fatty acid and alcohol molecules are amphipathic molecules and monolayers or multilayers of these types of molecules would arrange in such a manner that the hydrophilic groups are buried into a medium of higher dielectric constant. Thus, the surface of the layer exposed to air would be essentially hydrophobic. When the water approaches this surface, however, there will be a tendency for the hydrophilic groups to turn towards the water. This does not mean that the molecules are becoming static facing one way or the other but that they are in a dynamic equilibrium and at any moment a certain fraction faces the water surface and the remaining faces the bulk of its own kind. Thus, one can visualize a shift in equilibrium of the molecular orientation when the water comes in contact with the acid surface. The rate at which the new equilibrium is established depends on the mobility of the molecules of the solid. For liquids, solids of short molecular chains, and monomolecular layers, equilibrium is established

rather fast but for three-dimensional solids (multimolecular layers) the rate is quite slow depending on the length of the molecule.

At first, it seems rather difficult for molecules in a well-packed layer to find enough room for overturning. This requires the molecules to be rather flexible; skeleton films (films of stearic acid and calcium stearate from which the stearic acid has been dissolved), however, contain as much as 40% of voids and indicate extraordinary rigidity since they do not collapse. As Langmuir (27) points out, the molecules can be either flexible or rigid depending on the position that they occupy. Mack's (47) model for the stearic acid molecule indicates that, when the model is set on a flat surface, its carbon atoms can be arranged in a zigzag pattern. As long as the molecule rests on a flat surface it acts as a rigid body. If, however, it is lifted from the flat surface, it can be rolled almost into a sphere or into a great variety of other shapes. The molecules are in constant thermal disturbance and vibration and once they are released from the restraint of their neighbors they can roll and find themselves facing the direction of the water where the hydrophilic groups can be dissolved. If molecules can escape the solid and cause vapor pressure they can certainly rotate when occasion arises.

The stearic acid molecule can be pictured as a cylinder with a radius of 2.52\AA . If this molecule is rolled into a sphere its radius is 4.9\AA . X-ray studies (33) have shown that the molecules of stearic acid in a crystal are 3.7 to 4\AA apart or a total radius as high as 6.5\AA per molecule. This is adequate for molecular movements. The spherical configuration of the molecule discussed here is an extreme case and should

not be considered as the intermediate form of the molecule upon reorientation. The actual shapes taken by the molecules are probably numerous and in all probability very unsymmetrical. It cannot be claimed that each molecule operates independently but it is conceivable that the movement of one molecule will trigger others to break bonds from their neighbors and rotate or take other appropriate positions.

Molecular reorientation of the acid molecules explains the experimental observations presented earlier. The change in the contact angle with interfacial aging has to be due to molecular reorientation since it is not due to moisture adsorption and spreading of the solid. The fact that all three acids considered show the same equilibrium contact angle is strong evidence that molecular movements of the solid take place to provide a solid surface composed of either carboxyl or methyl groups. The reorientation of the top molecular layer of the acid cannot be considered complete since such a reorientation would render a surface which would be completely wettable. It can be visualized that the carboxyl groups of the top molecular layer of the acid surface are attracted by water and by similar carboxyl groups lying under the top molecular layer. Each carboxyl group would spend part of the time in contact with water and the remainder of the time in contact with another carboxyl group of the acid. The fraction of the time spent in each position depends on the forces between the interfaces at equilibrium. It remains now to attempt calculations, using the data of this investigation, to relate the contact angle to the number of molecules facing the water surface at any time after the initial contact with water.

THE RATE OF REORIENTATION

If quantitative calculations are to be made, the hydrophobic contact angle must be related to the composition or the orientation of the film. An approach to this problem can be made by assuming that the total work of adhesion of water on the acid surface is composed of contributions by each grouping exposed to the surface. Thus, for a compact and vertically oriented film the work of adhesion (\underline{W}_A) per square centimeter at any moment will be

$$\underline{W}_A = x \underline{W}_{\text{COOH}} + (1-x) \underline{W}_{\text{CH}_3} \quad (30)$$

where x is the fraction of the surface composed of carboxyl groups. It was shown earlier that the work of adhesion (\underline{W}_A) of a liquid on a solid is given by

$$\underline{W}_A = f_{\text{SV}^0} + \gamma_{\text{LV}^0} (1 + \cos \theta) \quad (31)$$

where f_{SV^0} is the decrease in surface energy of the solid upon exposure to an atmosphere saturated with the liquid, γ_{LV^0} is the surface tension of the liquid and θ is the contact angle of the liquid on the solid. As shown in Appendix IV, manipulation of Equations (30) and (31) results in the following simple useful equation:

$$\underline{x} = (\cos \theta_x - \cos \theta_0) / (\cos \theta_1 - \cos \theta_0) \quad (32)$$

where,

\underline{x} = fraction of molecules reoriented or fraction of area composed of COOH groups

θ_0 = contact angle at $\underline{x} = 0$ or the contact angle before any re-orientation occurs ($-\text{CH}_3$ surface)

θ_1 = contact angle at $\underline{x} = 1$ or the contact angle after all the molecules are reoriented (-COOH surface)

$\theta_{\underline{x}}$ = contact angle at any degree of reorientation (surface composed of CH_3 and COOH groups)

An expression similar to (32) has been derived by Zisman and Shafrin (48) for the fraction of a solid covered with a hydrophobic layer on the degree of compaction of the molecules adsorbed on the solid. All $\underline{x} = 0$ all the molecules are presumably endotropic and the contact angle will be equal to that of paraffin, i.e., $\theta_0 = 105^\circ$; the experimental contact angle for stearic acid before interfacial aging is about 105° . At $\underline{x} = 1$ all the molecules are exotropic (face the water) and θ_1 is zero. There are no experimental data for contact angles on surfaces composed solely of carboxyl groups since no such surface can be formed and stay that way but it is generally believed (1, 34) that a surface composed of carboxyls and hydroxyls would be completely wettable. Thus, using $\theta_0 = 105^\circ$ and $\theta_1 = 0$, Equation (32) reduces to

$$\underline{x} = 0.784 \cos \theta_{\underline{x}} + 0.216 \quad (32a)$$

which shows that the degree of reorientation is related linearly to the cosine of the contact angle.

Using the equilibrium contact angles for stearic, myristic, and lauric acid the degree of reorientation at equilibrium is 47.1, 48.4, and 49.7%, respectively. It will be recalled that the degree of reorientation for all fatty acids was expected to be 50%. The experimental results for the three acids studied are in excellent agreement with this general conclusion. The figure 50% compares favorably with the 50% transfer

which occurred when a monolayer of stearic acid deposited on a solid came in contact with another clean and identical solid (21). Here the two surfaces (water and carboxyl groups) are not identical but they are similar.

Rideal and Tadayon (21) suggest that the reaction of molecular reorientation is unimolecular. If the assumption is made that the reaction is reversible and unimolecular, the rate of reorientation should be described by

$$\frac{dx}{dt} = k'(1-x) - \frac{k_r}{x} \quad (33)$$

where k' and $\frac{k_r}{x}$ are the forward and reversible rate constants, t is time, and x is the fraction of molecules overturned at any time t . At equilibrium, $\frac{dx}{dt}$ is equal to zero and the above expression can be integrated to

$$(1-x/x_e) = \exp(-k't/x_e) \quad (34)$$

where x_e is the degree of reorientation at equilibrium and the other symbols have the meaning explained above.

If Equations (32) and (34) are combined, an expression relating the rate constant to the contact angle is obtained:

$$\log(\cos\theta_e - \cos\theta_x) = -k't/(2.303x_e) + \log[x_e(\cos\theta_1 - \cos\theta_0)] \quad (35)$$

where θ_e is the contact angle at equilibrium and the other symbols have the same meaning as before. Appendix IV shows the individual steps involved in deriving equation (35). This expression shows that, if $\cos\theta_e -$

$\cos \theta_x$ is plotted versus t on semilogarithmic paper, a straight line is obtained with a slope equal to $-k'/2.303x_e$. Figure 7 shows the data, obtained for the wettability of stearic acid at different temperatures, plotted in this manner. Figure 8 is a similar plot for the data obtained studying the wettability of myristic acid at one temperature. The relatively good fit of the data into this form indicates that the above expression is descriptive of the phenomenon of molecular reorientation.

Table XI shows the experimental rate constants for the wetting of stearic acid multilayers at different temperatures.

TABLE XI
EXPERIMENTAL RATE CONSTANTS FOR STEARIC ACID
AT DIFFERENT TEMPERATURES

Temperature, °C.	Rate Constant, sec. ⁻¹
13.5	5.06 x 10 ⁻⁶
15.5	6.81 x 10 ⁻⁶
23.0	2.46 x 10 ⁻⁵
25.0	2.62 x 10 ⁻⁵
28.5	7.05 x 10 ⁻⁵

The rate constant for myristic acid at 25°C. is 3.13×10^{-3} sec.⁻¹. Then rate constants for both acids compare favorably with the constants predicted by the absolute reaction rate theory shown in Table I, page 35.

The kinetics of a reaction can be described by the classical Arrhenius equation

$$k' = A \exp (-E/RT) \quad (36)$$

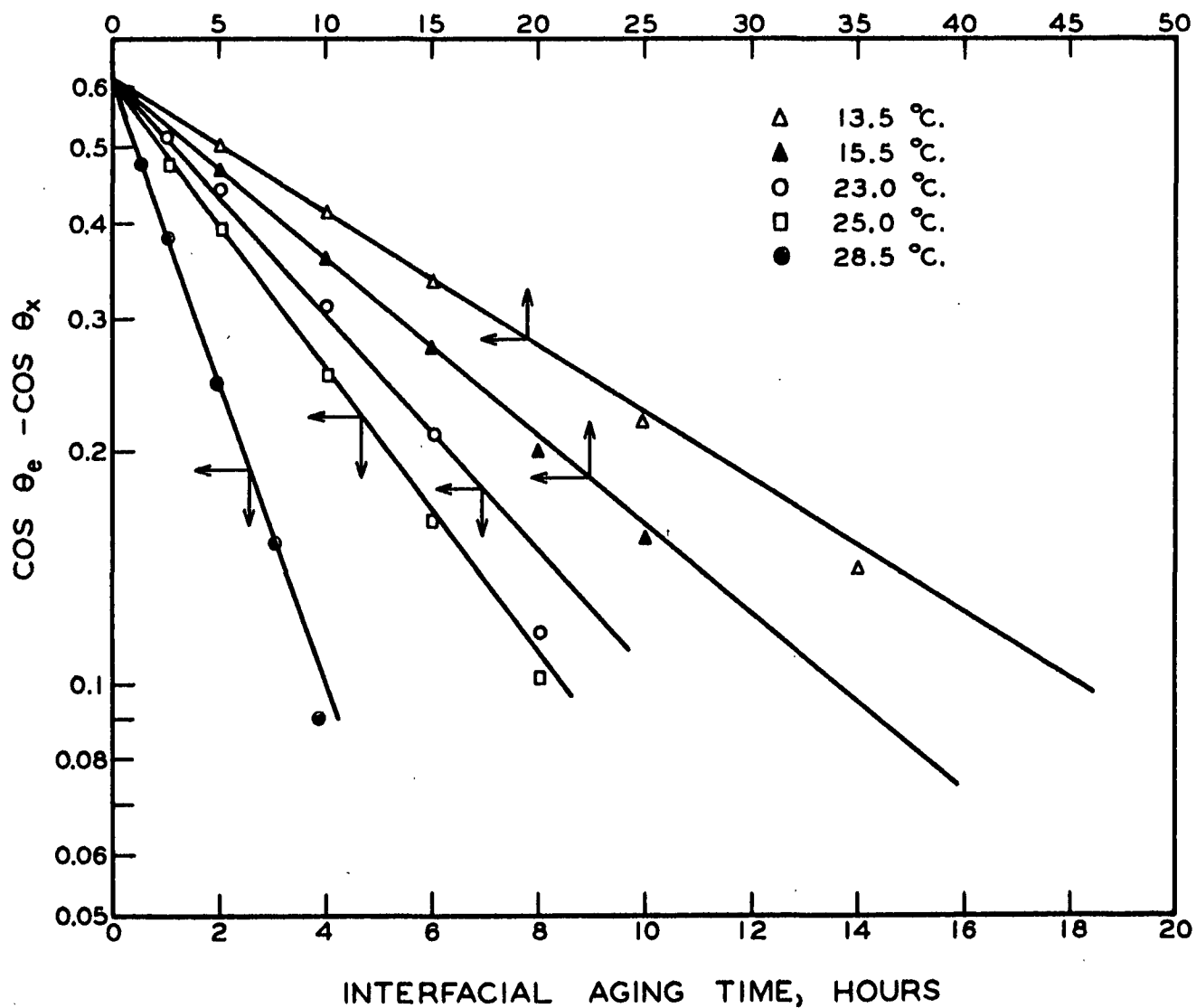


Figure 7. The Effect of Aging on the Wettability of Stearic Acid at Different Temperatures

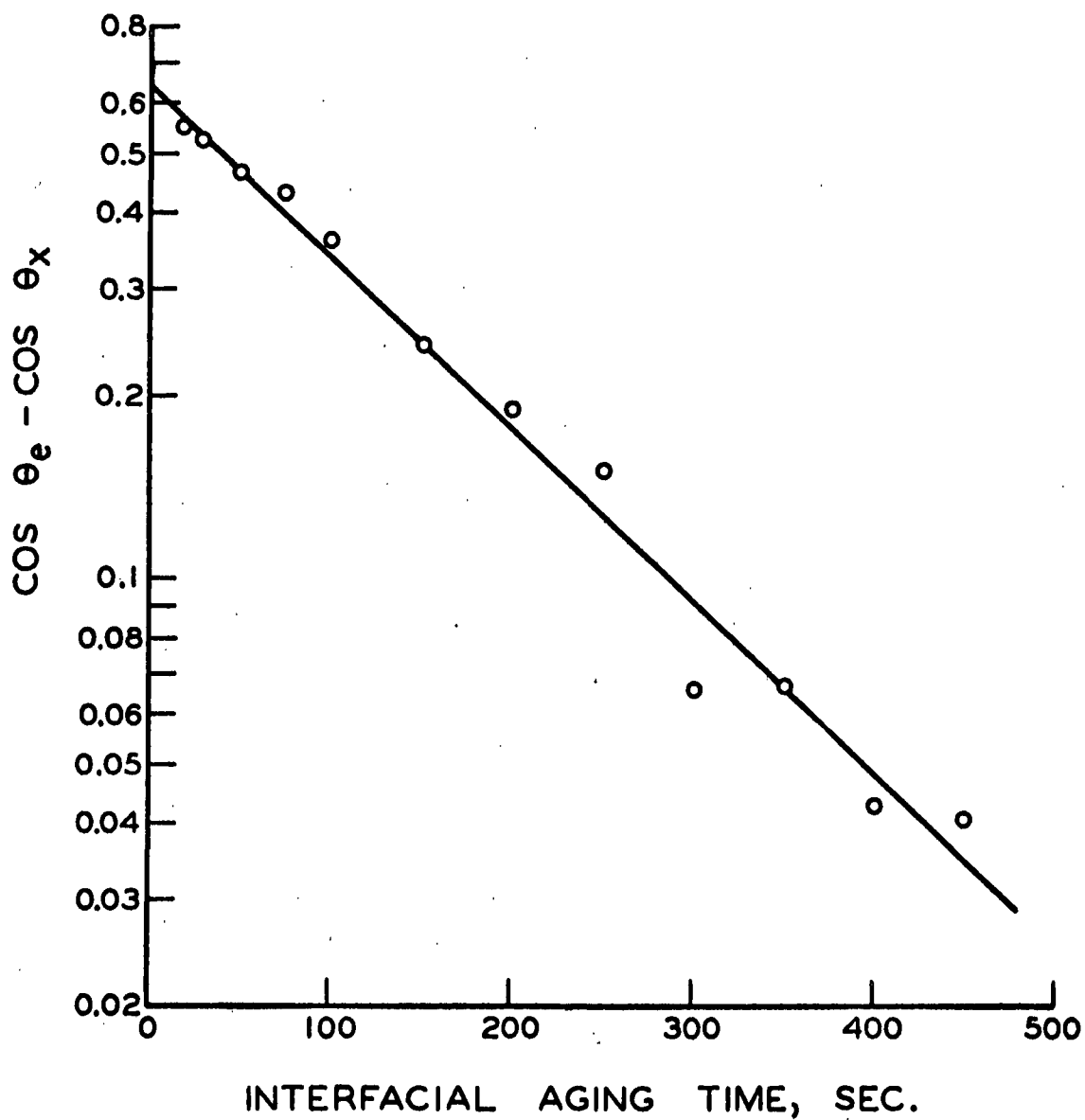


Figure 8. The Effect of Aging on the Wettability of Myristic Acid at 25°C.

where k' is the rate constant, A is a constant, R is the gas constant, T is the absolute temperature and E is the experimental energy of activation. This equation shows that if $\log k'$ is plotted versus $1/T$ a straight line results with a slope equal to $-E/(2.303R)$. Such a plot allows for the determination of the energy of activation involved in the reaction. If this is done for the data on the wettability of stearic acid at different temperatures a straight line results as shown in Fig. 9. The two points which seem to be out of line are for the temperatures 30 and 35°C. where some transition of the surface seems to take place. These two points have been estimated from the initial rates of the contact angle. Consequently, only the slope of the line formed by the points below 30°C. is considered to be reliable. The plot for the range of temperature between 13 and 30°C. shows that the energy of activation for the wettability of stearic acid is $27,558 \pm 850$ cal./mole. It will be recalled that the energy of activation was assumed to be equal to the cohesive energy of the acid, i.e. 25,000 cal./mole. The two figures seem to be in fair agreement.

Eyring's theory of absolute reaction (49) is an attempt to improve the Arrhenius equation by evaluating the constant A or the frequency factor which seems to depend on the temperature. The most common form of this theory, which was presented earlier is

$$k' = (kT/h) \exp(-\Delta F^*/RT) \text{ or } k' = (kT/h) \exp\left[(-\Delta H^*/RT) + (\Delta S^*/R)\right] \quad (37)$$

where

ΔF^* = free energy of activation

k = Boltzmann constant

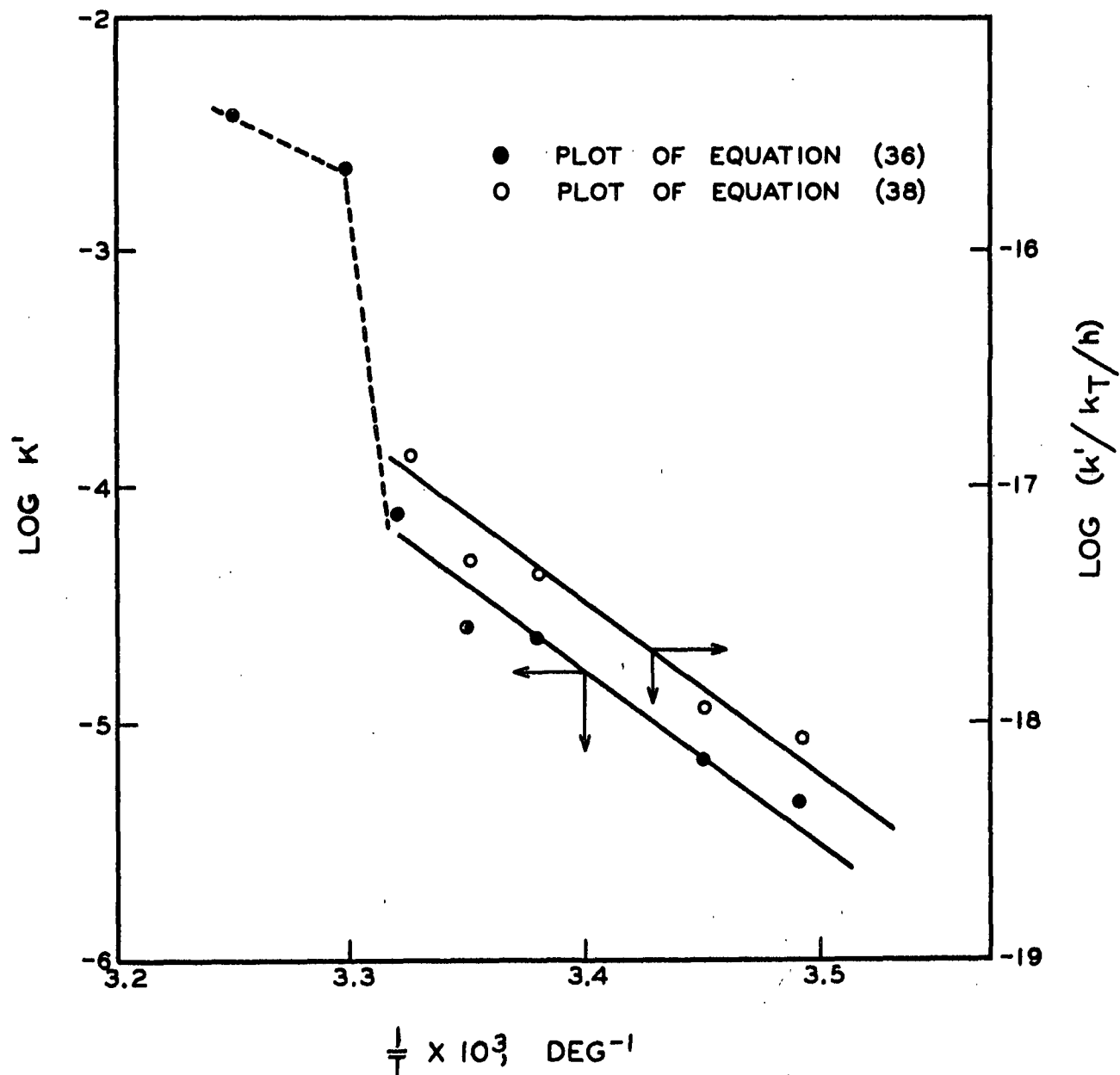


Figure 9. Determination of Energy of Activation For the Wettability of Stearic Acid

\underline{h} = Planck's constant

$\Delta \underline{H}^*$ = energy of activation

$\Delta \underline{S}^*$ = entropy of activation

\underline{R} = gas constant

\underline{T} = absolute temperature

The quantity $\Delta \underline{H}^*$ has been shown to be equal to $\underline{E} - \underline{RT}$ (49) and the Eyring expression can be transformed to read

$$\log(\underline{k}'/\underline{kT}/\underline{h}) = \left[\left\{ (\Delta \underline{S}^*/\underline{R}) + 1 \right\} / 2.303 \right] - \underline{E}/(2.303 \underline{RT}) \quad (38)$$

Equation (38) allows for the evaluation of an intercept which is independent of the temperature and contains the entropy of activation. When the data for the wettability of stearic acid at different temperatures are treated according to this equation the following simplified form is obtained:

$$\log(\underline{k}'/\underline{kT}/\underline{h}) = 3.0121 - 6.043.4/\underline{T} \quad (39)$$

The entropy of activation can be calculated to be 11.8 ± 3.0 entropy units. The positive change in entropy is a measure of the disorder which occurs when the molecules of the top layer overturn. The disorder is significant but it is far from the disorder occurring when the molecules are completely vaporized. The entropy is comparable to values obtained for certain flow and diffusion processes (49).

The entropy of activation involved during the process of molecular reorientation increases the rate since this quantity appears as a positive exponent in the kinetic equation (37). The entropy of activation would be

expected to be ~~s~~smaller for acids with smaller molecular length. This investigation, however, has no data to confirm this expectation. It appears that the rate of reorientation depends on the cohesive energy of the molecules and the disorder occurring during the breaking of the bonds of each molecule from its neighbors. Both these properties depend on the molecular length of the acid.

GENERAL SUMMARY

The principal objective of this investigation has been to provide further evidence which will strengthen or weaken the hypothesis that when water comes in contact with a solid fatty acid the top molecular layer reorients itself so as to increase the wettability of the surface. A further objective of this thesis has been the study of the kinetics of such reorientation.

The problem was tackled theoretically by using the Maxwell-Boltzmann statistical distribution to determine the probability of reorientation at equilibrium. It turns out that 50% of the molecules at the top molecular layer of any fatty acid would reorient themselves so that the carboxyl groups would face the water. The rate of reorientation can be estimated by the use of the theory of absolute reaction rate assuming the energy of activation to be equal to the cohesive energy of the molecules of the acid. Thus, the rate of reorientation depends on the length of the molecule.

The experimental approach to the problem consists of studying the wettability of both monolayers and multilayers of fatty acids on solids. Special effort was made to prepare a surface with a monolayer having variable fractions of molecules which are capable of any mobility. Thus, having such a surface one can attribute changes in the contact angle with interfacial aging to the mobility of the molecules of the acid and possibly to the reorientation of the molecules. Such a surface was prepared by depositing mixed monolayers of stearic acid and stearyl alcohol of variable

concentration on a copper surface. The acid molecules react with the copper becoming immobile while the stearyl alcohol molecules are only adsorbed and thus capable of mobility. The same type of surface was prepared by depositing a stearic acid monolayer on a silver substrate and allowing it to age for different time intervals. The stearic acid reacts with the silver substrate very slowly thus providing a surface with different fraction of molecules capable of any movement and re-orientation. The equilibrium contact angles of water on such surfaces correlated well with the mobile fraction of the molecules in the monolayer. Experiments with such monolayers showed that the reduction in the contact angle was not due to spreading of the monolayer on the water droplet but to reorientation at the interface. The contact angle of water on an immobile monolayer is practically the same as that on paraffin and does not change with interfacial aging.

The wettability of multilayers of stearic, myristic, and lauric acid was low initially but increased upon interfacial aging. The contact angle was the same for the three surfaces at equilibrium. This is an indication that the molecules of the acid at the interface reorient when in contact with water for a considerable time. The rates at which the equilibria were attained, however, were different depending on the molecular length of the acid. For stearic acid, ~~equilibrium is established in about~~ ten hours while for lauric acid only a few seconds are necessary. The wettability of multilayers of stearic acid was studied at different temperatures in order to obtain data required for a kinetic study of the re-orientation process. The rate of the reaction increased normally up to

30°C. but at this temperature there seems to be some sudden increase in the rate, indicating some type of surface transition.

The surface composition of the acid multilayer was related to the contact angle for the purpose of estimating the number of molecules re-oriented at equilibrium or at any time of interfacial aging. It was found that approximately 50% of the molecules of the acid reorient themselves so that the carboxyl groups will dissolve in the water phase. This is in excellent agreement with the results predicted by the Maxwell-Boltzmann statistical distribution.

The study of wettability at different temperatures allowed determination of the energy and entropy of activation for the wetting reaction. The results show that the experimental energy of activation for stearic acid is about 27,000 cal./mole as compared to 25,000 cal./mole which is the cohesive energy of stearic acid. The fair agreement between the two values indicates that the kinetics of the reaction is determined by the cohesive energy or the length of the molecule. The entropy of activation for the wetting of stearic acid is about 11 entropy units showing the disturbance or the disorder occurring in the monolayer during orientation. It should be emphasized that the molecules are not pictured as stationary with the carboxyl groups facing one way or the other but rather as a dynamic phenomenon with a fraction of the carboxyls facing the water side of the interface while the remaining fraction of molecules face the bulk of the acid itself.

CONCLUSIONS

The conclusions of this investigation can be stated as follows:

1. The wettability of fatty acids increases with prolonged water contact. The wettability of paraffin or acid monolayers which have been allowed to chemically react with the solid substrate, remains practically unchanged.
2. The wettability of mixed stearic acid-stearyl alcohol monolayers increases with increasing alcohol content when the substrate reacts chemically with the acid but remains unchanged when the substrate does not react with the acid.
3. Moisture in amounts found in saturated air cannot appreciably alter the wettability of hydrophobic surfaces of stearic acid, stearyl alcohol, and paraffin.
4. Stearic, myristic, and lauric acid show the same equilibrium contact angle but the rates at which the equilibria are attained are different. The rates are definitely related to the size of the molecules involved.
5. While moisture adsorption and solid spreading can be important factors contributing to the increase in wettability with interfacial aging, it is concluded that they are not the predominant factors in the present investigation. The results, however, can satisfactorily be interpreted on the basis of molecular re-orientation at the solid surface.

6. Theoretical considerations, utilizing the Boltzmann statistical distribution and interfacial tensions, show that 50% of the molecules in the top molecular layer of fatty acid multilayers should reorient themselves when wetting equilibrium is established. Treatment of the experimental data reveals about 50% reorientation in the top molecular layer of stearic, myristic, and lauric acid.
7. The rates at which the wetting equilibria are established are related to the molecular mobilities of the acids. The energy of activation for the wetting of stearic acid is about 27,000 cal./mole which is the cohesive energy for the same acid. A fair estimate of the rate of reorientation can be made by using the absolute reaction rate theory and equating the energy of activation to the energy of cohesion of the solid acid.

SOME APPLICATIONS AND SUGGESTIONS FOR FURTHER WORK

The subject of wetting is a very important one in many industries where water-resistant materials are manufactured. Industries making products where absorption is the desired quality are also interested in the same wetting principles. Here only applications with reference to the paper industry will be discussed. The end uses of paper products call for both sized and absorbent types of papers. The sizing agents normally used are amphipathic molecules which have the ability to adsorb on the cellulose fibers and decrease the surface energy of the paper. The phenomenon of self-sizing (the loss of absorbency of paper as the paper ages) has been attributed to the amphipathic molecules present in the ray cells of most wood species (50). The fatty and resin acids migrate out of the ray cells and distribute themselves throughout the fibers where they can be adsorbed and decrease the free surface energy of the cellulosic fibers.

Water resistance is usually judged by the rate at which wettability occurs rather than by the equilibrium condition. Thus, the equilibrium contact angle may be rather low or even zero but if the time taken to reach equilibrium is long the product can be considered as water-resistant and suitable for a particular purpose. In making water-resistant products it is the end use which will dictate whether the kinetics or the equilibrium of the wetting is the controlling factor.

The present investigation has concentrated on the wetting rather than penetration and absorption of water into solids. Ordinarily a

surface must be wetted before penetration occurs. Molecular reorientation of a sizing agent increases wetting and it will invariably increase penetration of water into the porous solid. From the results of this investigation it is apparent that a good sizing agent must, in addition to being sorbed on the fiber and reduce its free energy, possess at least one of the following fundamental properties:

1. The molecules of the sizing agent may have high energy of cohesion either by the nature or the size of the molecule. This will increase the energy of activation and consequently will decrease the rate of reorientation.
2. The molecules may react or polymerize among themselves so that their mobility becomes negligible and the rate of reorientation decreases considerably.
3. The molecules may undergo chemical reaction with the cellulosic surface so that they become immobile. This would increase the stability of sizing considerably.

Anything that would decrease the mobility of the molecules of the sizing agent in paper would improve sizing. The relatively new sizing agent with alkylketene dimer (Aguapel) seems to be an application of chemical reaction of the sizing agent with the cellulose surface. The traditional rosin sizing agent may be an application of polymerization of the aluminum monoabietate to create giant molecules of minimum mobility (40). The giant molecule of a sizing agent must either be formed after the agent is sorbed by the fiber

or before applied to the paper. Efforts in forming a large molecule before application to the paper have shown promising results in a sizing agent presently under development (51).

Future research must concentrate in finding the ideal molecule for a sizing agent. This may well be a simple molecule but it must be versatile, easy to use, must not reduce the strength of the paper, must be picked up by the cellulosic fibers, and above all it must anchor itself strongly so that it cannot move and reorient itself when it comes in contact with the polar liquid.

The unsolved problems in the phase of the industry where absorbent papers are manufactured are numerous. The removal of the hydrophobic fatty and resin acids or a treatment which will inhibit their reactivity with the cellulose or increase their mobility are the two main avenues for solving such problems. Treatment which would polymerize the resin and fatty acids while still in the ray cells or form a film around the ray cells to prevent migration may be the desired answer. Separating the ray cells from the pulp would not only remove the cause to loss in absorbency but would also provide a source of fatty and resin acids. Thus, removal of the ray cells may be economically practical.

The behavior of monolayers on various solids is not completely understood. Means must be found to measure the energy of adhesion of a monolayer on a solid. Such means may allow for finding out the anchoring ability of a molecule on cellulose. The effect of temperature on the disorientation of the monolayer must be pursued further. Menter and Tabor (52) have done some

work on the disorientation of monolayers by the use of electron diffraction but no such study appears to have been made on the disorientation at the surface of multilayers. The present investigation has indicated a transition on the top molecular layer of a stearic acid surface at a rather low temperature. This, however, cannot be considered conclusive.

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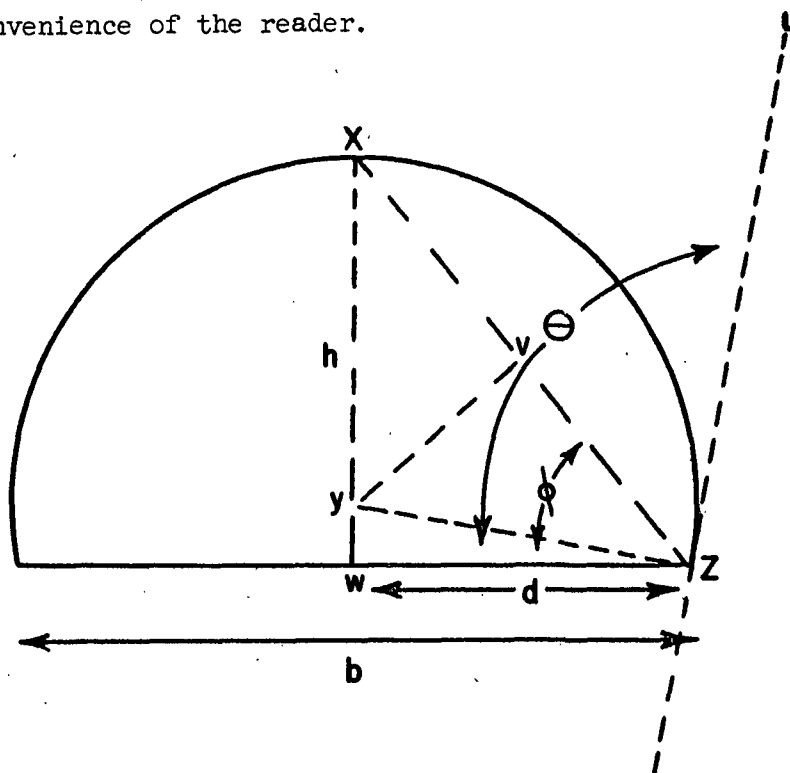
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APPENDIX I

DERIVATION OF EQUATION USED TO CALCULATE CONTACT ANGLES

The derivation is given by Guide (40) but it is shown here only for the convenience of the reader.



$$\tan \frac{1}{2} \Theta = 2h/b$$

The derivation of this equation is as follows:

$$\angle_{wyz} + \angle_{yzw} = 90^\circ \quad (1)$$

$$\angle_{xyz} + \angle_{wyz} = 180^\circ \quad \text{therefore,} \quad (2)$$

$$\angle_{xyz} - \angle_{yzw} = 90^\circ \quad (3)$$

$$\angle_{yzu} = 90^\circ \quad \text{therefore,} \quad (4)$$

$$\angle_{xyz} - \angle_{yzw} = \angle_{yzu} \quad \text{or,} \quad (5)$$

$$\angle_{xyz} = \angle_{yzu} + \angle_{yzw} = \theta \quad (6)$$

$$\angle_{vyz} + \angle_{vzy} = 90^\circ \quad (7)$$

Therefore, adding (1) and (7),

$$\angle_{vzy} + \angle_{yzw} + \angle_{vyz} + \angle_{wyz} = 180^\circ \quad (8)$$

$$\angle_{xyv} + \angle_{vyz} + \angle_{zyw} = 180^\circ \quad (9)$$

therefore,

$$\angle_{yzw} + \angle_{vzy} = \angle_{xyv} \quad (10)$$

but,

$$\angle_{yzw} + \angle_{xzy} = \phi, \quad (11)$$

and,

$$\angle_{xyv} = 1/2 \angle_{xyz} = (1/2)\theta \quad (12)$$

therefore,

$$\phi = 1/2\theta \quad (13)$$

$$\tan \phi = \frac{h}{d} = \frac{h}{1/2b} = \frac{2h}{b} \quad (14)$$

therefore,

$$\tan(1/2)\theta = \frac{2h}{b} \quad (15)$$

EVALUATION OF THE METHOD OF MEASURING THE ANGLE OF CONTACT

A paraffin layer (m.p. 69.3°C.) was deposited on a glass microscope slide and the pictures of droplets were taken at 20 seconds interfacial aging. The angle of contact was measured by the use of the formula $\tan(\theta/2) = 2h/b$ (θ indirect) and by just drawing tangents on the photograph (θ direct). A comparison of the two methods is given below:

<u>Droplet</u>	<u>Indirect</u>	<u>Direct</u>
1	105.5	104.0
2	106.0	107.0
3	105.0	108.0
4	105.0	104.0
5	104.0	106.0
6	106.3	105.0
7	106.0	107.0
8	104.0	103.0
9	105.3	108.0
10	<u>106.2</u>	<u>105.0</u>
$\Sigma \theta$	1053.3	1057.0
$\Sigma \theta^2$	110,950.05	111,753.0
\underline{n}	10	10
$\theta_{av.}$	105.3	105.7
θ^2	0.71	3.11
θ	0.84	1.76

APPENDIX II

REPRODUCIBILITY AND STABILITY OF MONOLAYERS

This appendix shows the data obtained during the preliminary work of this investigation which was designed to study the deposition characteristics of monolayers and multilayers on different substrates. The use of radioactive material facilitates the characterization of the monolayers. The objective of this work was pointed towards the reproducibility and stability of the molecular layers.

TABLE XII

MONOLAYERS OF STEARIC ACID ON COPPER SLIDES BY THE
BENZIDINE METHOD OF DEPOSITION (0.06 μ c./mg.)

Run	Copper Slide	Radioactive Count, c.p.m.
A	1	68.4
	2	73.9
	3	65.5
		<hr/> 69.3 \pm 2.7
B	1	69.3
	2	68.9
	3	73.0
	4	73.8
	5	75.3
Average		<hr/> 72.0 \pm 2.1

TABLE XIII

MONOLAYERS OF STEARIC ACID ON DIFFERENT SUBSTRATES
BY THE BENZIDINE METHOD (1.64 μ c./mg.)

Slide No.	Copper Slide	Silver Slide	Glass Slide
1	1398	1270	1130
2	1192	1200	1100
3	1250	1251	1126
4	1229	1230	1092
5	1330	1282	1038
6	1275	1240	1025
7	1295	1260	1090
Average	1281.0 c.p.m.	1248.0 c.p.m.	1086.0 c.p.m.
Backscattering Coefficient	1.179	1.149	1.0

All the materials should give the same counting since the same amount of surface film is transferred from the water surface to the solid substrate; this is not so for the reason that the different substrates have varying back-scattering coefficients. These coefficients can be calculated with respect to one of the substrates. Glass has been chosen as reference in this case.

TABLE XIV

DEPOSITION OF MULTILAYERS ON SILVER AND COPPER SLIDES
BY THE BENZIDINE METHOD ($1.64 \mu \text{ c./mg.}$)

Slide No.	No. of Monolayers	Copper Substrate	Silver Substrate
1	7	8970	8754
2	7	8891	8667
3	7	8902	8723
Average		<u>8914.3 c.p.m.</u>	<u>8714.6 c.p.m.</u>
Counts/Monolayer		1273.5 c.p.m.	1244.9 c.p.m.

Note: Comparison of Tables XIII and XIV shows that deposition of monolayers and multilayers by the benzidine method is reproducible.

TABLE XV

DEPOSITION OF STEARIC ACID AND STEARYL ALCOHOL MONOLAYERS
ON COPPER AND GLASS SUBSTRATES FROM PURE WATER

Slide No.	Stearic Acid, $1.64 \mu \text{ c./mg.}$		Stearyl Alcohol, $0.88 \mu \text{ c./mg.}$	
	Copper	Glass	Copper	Glass
1	1411	1012	610	572
2	1406	1097	670	520
3	1361	1200	692	552
4	1481	1169	645	530
5	1395	962	630	594
6	1391	842	625	572
7	----	1251	680	612
8	----	1089	712	515
Average (c.p.m.)	<u>1392.0</u>	<u>1078.0</u>	<u>658.0</u>	<u>558.4</u>

Note: Table XV shows that monolayers can be deposited successfully from pure water. An attempt to deposit multilayers in the above manner, however, was unsuccessful.

TABLE XVI

DEPOSITION OF MIXED MONOLAYERS ON
COPPER FROM PURE WATER

Radioactive Stearyl Alcohol, %	Inactive Stearic Acid, %	Counts, d.p.m.
0	100	10
32	68	205
48	52	310
65	35	423
100	0	650

Table XVI shows that mixed monolayers of stearic acid and stearyl alcohol can be deposited from pure water and the counting is proportional to the amount of radioactive alcohol present.

TABLE XVII

DESORPTION OF STEARIC ACID MONOLAYERS
IN BENZENE^a AT 25°C.

Aging ^b After Deposition, hr.	Initial Counts, c.p.m.			Final Counts, c.p.m.		
	Copper	Silver	Glass	Copper	Silver	Glass
0	1350	1280	1060	515	95	20
2-3/4	1350	1280	1060	910	102	15
5	1350	1280	1060	1010	100	31
24 ^c	1350	1280	1060	1150	110	28
48	1350	1280	1060	1174	113	23

^a The desorption was carried out by dipping the slide into 50 cc. benzene at 25°C. for 10 min.

^b Aging means allowing the sample to stand over CaCl₂ in a desiccator prior to dipping into benzene.

^c A spot experiment with stearyl alcohol on the three substrates at 24-hour aging after deposition showed that the stearyl alcohol monolayers could be completely removed with benzene.

TABLE XVIII

DESORPTION OF STEARIC ACID MONOLAYERS IN WATER^a

Substrate	Initial Counting, c.p.m.	Time of Immersion	Temp. °C.	Final Counting, c.p.m.
Glass	1138	30 min.	25	1050
"	"	3 hrs.	25	957
"	"	18 hrs.	25	907
"	"	19 hrs.	39	642
	1127	24 hrs.	39	625
	1093	24 hrs.	50	434

^a The slides were dipped into 100 cc. of water and were removed in such a manner that no redeposition from the water surface was possible. This was accomplished by enclosing the slide with an aluminum foil before removal from the water.

APPENDIX III

RELATION OF CONTACT ANGLE AND SURFACE COMPOSITION

An approach to the problem can be made by assuming that the total work of adhesion (\underline{W}_A) of a liquid to a solid surface is composed of contributions by each grouping exposed to the surface. For a compact and vertically oriented film the work of adhesion at any moment will be

$$\underline{W}_A = \underline{W}(\text{COOH}) + \underline{W}(\text{CH}_3) \quad (30)$$

Let us define the composition of the film by

$$\underline{x} = \text{carboxyl content} = \frac{(\text{COOH})}{(\text{CH}_3) + (\text{COOH})} \quad (30-1)$$

$$\underline{y} = \text{methyl content} = 1 - \underline{x} = \frac{(\text{CH}_3)}{(\text{CH}_3) + (\text{COOH})} \quad (30-2)$$

Equation (30) can be simplified by making the reasonable assumption that each component term can be expressed as the product of a constant \underline{K}_i specific to the exposed species \underline{i} , multiplied by the appropriate fraction of projected surface area.

$$\underline{W}_A = \underline{K}_i \underline{A}_i \quad (30-3)$$

Thus, Equation (30) can be written as

$$\underline{W}_A = (\underline{A} \cdot \underline{K})_{\text{COOH}} + (\underline{A} \cdot \underline{K})_{\text{CH}_3} \quad (30-4)$$

But for vertical orientation of a compact film, Equation (30-4) can be altered to

$$\underline{W}_A = (\underline{x} \cdot \underline{K})(\text{COOH}) + (1 - \underline{x}) (\underline{K})_{\text{CH}_3} \quad (30-5)$$

$$\text{or } \underline{x} = \frac{\underline{W}_A - \underline{K}(\text{CH}_3)}{\underline{K}(\text{COOH}) - \underline{K}(\text{CH}_3)} \quad (30-6)$$

At a given solid-liquid interface where the angle of contact $\theta \neq 0$, \underline{W}_A is given by

$$\underline{W}_A = \underline{f}_{\text{sv}^0} + \gamma_{\text{LV}^0} (1 + \cos \theta_E) \quad (31)$$

where $\underline{f}_{\text{sv}^0}$ is the decrease in surface energy upon exposure of the solid to a saturated atmosphere of the liquid in question.

Let $\underline{f} = \underline{f}_{\text{s}_0\text{v}^0}$ at $\underline{x} = 0$ and $\theta = \theta_0$

$\underline{f} = \underline{f}_{\text{s}_x\text{v}^0}$ at $\underline{x} = \underline{x}$ and $\theta = \theta_x$

$\underline{f} = \underline{f}_{\text{s}_1\text{v}^0}$ at $\underline{x} = 1$ and $\theta = \theta_1$

$$\underline{x} = \frac{(\underline{f}_{\text{s}_x\text{v}^0} - \underline{f}_{\text{s}_0\text{v}^0}) + \gamma_{\text{LV}^0}(\cos \theta_x - \cos \theta_0)}{(\underline{f}_{\text{s}_1\text{v}^0} - \underline{f}_{\text{s}_0\text{v}^0}) + \gamma_{\text{LV}^0}(\cos \theta_1 - \cos \theta_0)} \quad (31-1)$$

$\underline{K}(\text{CH}_3)$ and $\underline{K}(\text{COOH})$ are obtained from Equations (30-6) and (31) for the limiting values of $\underline{x} = 0$ and $\underline{x} = 1$. The term $\underline{f}_{\text{s}_x\text{v}^0}$ can be considered to be the sum of the two terms $(\underline{f}_{\text{sv}})_{\text{CH}_3}$ and $(\underline{f}_{\text{sv}})_{\text{COOH}}$. Therefore, one can write $\underline{f}_{\text{s}_x\text{v}^0} = \underline{x}\underline{f}_{\text{s}_1\text{v}^0} + (1-\underline{x})\underline{f}_{\text{s}_0\text{v}^0}$ (31-2)

It is suggested by Zisman and Shafrin (48) that Equation (31-2) is applicable to metals and textiles partially covered with hydrophobic matter.

Substituting Equation (31-2) into (31-1) one obtains the working equation (32)

$$\underline{x} = \frac{\cos \theta_x - \cos \theta_0}{\cos \theta_1 - \cos \theta_0} \quad (32)$$

Thus, the composition of the film (\underline{x}) can be expressed as a function of the contact angle (θ). An equation analogous to (32) has been derived by Zisman and Shafrin (48) for the degree of compaction of a film adsorbed on a solid surface from a solution.

APPENDIX IV

RELATION OF RATE CONSTANT AND CONTACT ANGLE

Assume a reversible reaction between states A and B of a monolayer, k' being the rate constant of



the forward reaction and k_r being the rate constant of the reversible one.

The rate of appearance of B at any time t is

$$\frac{dx}{dt} = k'(1-x) - k_r x \quad (32-2)$$

where x is the fraction in state B or the fraction of molecules reoriented at any time t . At equilibrium $\frac{dx}{dt} = 0$ and

$$k'(1 - x_e) = k_r x_e \quad (32-3)$$

Solving for k_r in (32-3) and substituting in (32-2)

$$\frac{dx}{dt} = k'(1 - x - k'x(1 - x_e)/x_e) \quad (32-4)$$

or

$$\frac{dx}{dt} = k'(x_e - x)/x_e \quad (33)$$

Solving (33) for $x = 0$ at $t = 0$ and $x = x$ at $t = t$, Equation (33-1) is obtained

$$(x_e - x)/x_e = \exp(-k't/x_e) \quad (33-1)$$

or

$$1 - x/x_e = \exp(-k't/x_e) \quad (34)$$

Substitution of x by its equivalent from Equation (32) into (34) results in

$$\exp(-k't/x_e) = 1 - \left[(\cos\theta_x - \cos\theta_o)/x_e (\cos\theta_1 - \cos\theta_o) \right] \quad (34-1)$$

Taking logarithms and rearranging (34-1), Equation (34-2) is obtained

$$\ln \left[\frac{x_e}{x_e} \cos\theta_1 + \cos\theta_o (1 - \frac{x_e}{x_e}) - \cos\theta_x \right] = -k't/x_e + \ln \left[\frac{x_e}{x_e} (\cos\theta_1 - \cos\theta_o) \right] \quad (34-2)$$

It is observed that $\frac{x_e}{x_e} \cos\theta_1 + \cos\theta_o (1 - \frac{x_e}{x_e})$ is a linear combination of the cosine of the equilibrium contact angle θ_e and Equation (34-2) is equivalent to (35)

$$\ln(\cos\theta_e - \cos\theta_x) = -k't/x_e + \ln \left[\frac{x_e}{x_e} (\cos\theta_1 - \cos\theta_o) \right] \quad (35)$$